

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 346 995 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
20.11.1996 Bulletin 1996/47

(51) Int Cl.⁶ C11D 3/37, C11D 10/04,
C11D 17/00

(21) Application number: 89201530.6

(22) Date of filing: 12.06.1989

(54) Liquid detergents

Flüssige Reinigungsmittel

Produits détergents liquides

(84) Designated Contracting States:
CH DE ES FR GB IT LI NL SE

• Van de Pas, Johannes Cornelis
NL-3136 CV Vlaardingen (NL)

(30) Priority: 13.06.1988 GB 8813978

(74) Representative: Kan, Jacob Hendrik, Dr. et al
Unilever N.V.
Patent Division
P.O. Box 137
3130 AC Vlaardingen (NL)

(43) Date of publication of application:
20.12.1989 Bulletin 1989/51

(60) Divisional application: 96200330.7 96200332.3

(73) Proprietors:

- UNILEVER N.V.
3013 AL Rotterdam (NL)
Designated Contracting States:
CH DE ES FR IT LI NL SE
- UNILEVER PLC
London EC4P 4BQ (GB)
Designated Contracting States:
GB

(56) References cited:

EP-A- 0 193 375	EP-A- 0 301 882
EP-A- 0 301 883	EP-A- 0 324 568
DE-A- 2 302 367	FR-A- 1 548 948
GB-A- 1 068 554	GB-A- 1 506 427
GB-A- 1 589 971	US-A- 3 235 505
US-A- 3 457 176	

(72) Inventors:

- Montague, Peter Graham
Rugby Warwickshire CV22 6QB (GB)

Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification

EP 0 346 995 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Lamellar droplets are a particular class of surfactant structures which, in general, are already known from a variety of references, e.g. "Anionic and Cationic Surfactants: Properties and Applications", Wiley, 1980.

US-A-3,924,568 discloses detergent compositions comprising a soapy material, alkylpolyalkylene glycol ether sulfate and copolymers of methyl methacrylate and maleic anhydride.

GB-A-1,968,554 discloses aqueous liquid detergent compositions comprising actives, salts and a polymer derived from a triethyleneglycol dimethacrylate-maleic anhydride copolymer as a structuring agent and as a second component an alkali-soluble terpolymer of maleic anhydride, maleic anhydride and a vinyl monomer.

EP-A-0,933,75 discloses liquid aqueous abrasive cleaners comprising polymers as structuring agents that provide a three-dimensional structure that functions as a network to suspend particles.

Non-published EP-A-932,456 discloses polymers of the generic formula $A(B)m(C)n(D)oE1$ for use in liquid detergent compositions in general.

US-A-3,285,005 discloses aqueous liquids comprising actives in the form of particles, individual droplets or emulsions, salt and a hydrolyzed acidic polymer material.

US-A-3,457,776 discloses aqueous liquid detergent compositions that comprise dispersed or emulsified detergent active material, salts and polymer material.

GB-A-1,506,427 and GB-A-1,589,971 disclose aqueous liquid detergent compositions that may comprise lamellar droplets and contain a co-polymer of maleic anhydride and vinylmethylether, ethylene or styrene, as a stabiliser.

FR-A-1,548,948 discloses aqueous liquid detergent compositions that may comprise lamellar droplets and from 0.0-5% by weight of a co-polymer of methyl ether vinyl and maleic anhydride, esterified with an zwitterionic surfactant.

Such lamellar dispersions are used to endow properties such as consumer-preferred flow behaviour and/or turbid appearance. Many are also capable of suspending particulate solids such as detergency builders or abrasive particles. Examples of such structured liquids without suspended solids are given in US patent 4 244 840, whilst examples where solid particles are suspended are disclosed in specifications EP-A-160 342; EP-A-38 101; EP-A-104 452 and also in the aforementioned US-A-4 244 840. Others are disclosed in European Patent Specification EP-A-151 884, where the lamellar droplet are called 'spherulites'.

The presence of lamellar droplets in a liquid detergent product may be detected by means known to those skilled in the art, for example optical techniques, various rheometrical measurements, X-ray or neutron diffraction, and electron microscopy.

The droplets consist of an onion-like configuration of concentric bi-layers of surfactant molecules, between which is trapped water or electrolyte solution (aqueous phase). Systems in which such droplets are close-packed provide a very desirable combination of physical stability and solid-suspending properties with useful flow properties.

The viscosity and stability of the product depend on the volume fraction of the liquid which is occupied by the droplets. Generally speaking, the higher the volume fraction of the dispersed lamellar phase (droplets), the better the stability. However, higher volume fractions also lead to increased viscosity which in the limit can result in an unpourable product. This results in a compromise being reached. When the volume fraction is around 0.6, or higher, the droplets are just touching (space-filling). This allows reasonable stability with an acceptable viscosity (say no more than 2.5 Pas, preferably no more than 1 Pas at a shear rate of 21 s^{-1}). This volume fraction also endows useful solid-suspending properties. Conductivity measurements are known to provide a useful way of measuring the volume fraction, when compared with the conductivity of the continuous phase.

Fig. 1 shows a plot of viscosity against lamellar phase volume fraction for a typical composition of known kind:

	wt. %
Surfactants	20
Na-formate	5 or 7.5
Na-citrate 2aq	10
Borax	3.5
Tinopal CBS-X	0.1

NaDoBS/LES/Neodol 23-6-5. See Table 3 in Examples for raw material specifications.

	wt %
Perfume	0.15
Water	balance

It will be seen that there is a window bounded by lower volume fraction of 0.7 corresponding to the onset of instability and an upper volume fraction of 0.83 or 0.9 corresponding to a viscosity of 1 Pas or 2 Pas, respectively. This is only one such pilot and in many cases the lower volume fraction can be 0.6 or slightly lower.

A complicating factor in the relationship between stability and viscosity on the one hand and, on the other, the volume fraction of the lamellar droplets is the degree of flocculation of the droplets. When flocculation occurs between the lamellar droplets at a given volume fraction, the viscosity of the corresponding product will increase owing to the formation of a network throughout the liquid. Flocculation may also lead to instability because deformation of the lamellar droplets, owing to flocculation, will make their packing more efficient. Consequently, more lamellar droplets will be required for stabilization by the space-filling mechanism, which will again lead to a further increase of the viscosity.

The volume fraction of droplets is increased by increasing the surfactant concentration and flocculation between the lamellar droplets occurs when a certain threshold value of the electrolyte concentration is crossed at a given level of surfactant (and fixed ratio between any different surfactant components). Thus, in practice, the effects referred to above mean that there is a limit to the amounts of surfactant and electrolyte which can be incorporated whilst still having an acceptable product. In principle, higher surfactant levels are required for increased detergency (cleaning performance). Increased electrolyte levels can also be used for better detergency, or are sometimes sought for secondary benefits such as building.

We have now found that the dependency of stability and/or viscosity upon volume fraction can be favourably influenced by incorporating a deflocculating polymer comprising a hydrophilic backbone and one or more hydrophobic side-chains.

The deflocculating polymer allows, if desired, the incorporation of greater amounts of surfactants and/or electrolytes than would otherwise be compatible with the need for a stable, low-viscosity product. It also allows (if desired) incorporation of greater amounts of certain other ingredients to which, hitherto, lamellar dispersions have been highly stability-sensitive. Further details of these are given hereinbelow.

The present invention allows formulation of stable, pourable products wherein the volume fraction of the lamellar phase is 0.5, 0.6 or higher, but with combinations or concentrations of ingredients not possible hitherto.

The volume fraction of the lamellar droplet phase may be determined by the following method. The composition is centrifuged, say at 40,000 G for 12 hours, to separate the composition into a clear (continuous aqueous) layer, a turbid active-rich (lamellar) layer and (if solids are suspended) a solid particle layer. The conductivity of the continuous aqueous phase, the lamellar phase and of the total composition before centrifugation are measured. From these, the volume fraction of the lamellar phase is calculated, using the Bruggeman equation, as disclosed in American Physics, 24, 636 (1935). When applying the equation, the conductivity of the total composition must be corrected for the conductivity inhibition owing to any suspended solids present. The degree of correction necessary can be determined by measuring the conductivity of a model system. This has the formulation of the total composition but without any surfactant. The difference in conductivity of the model system, when continuously stirred (to disperse the solids) and at rest (so the solids settle), indicates the effect of suspended solids in the real composition. Alternatively, the real composition may be subjected to mild centrifugation (say 2,000 G for 1 hour) to just remove the solids. The conductivity of the upper layer is that of the suspending base (aqueous continuous phase with dispersed lamellar phase, minus solids).

It should be noted that, if the centrifugation at 40,000 G fails to yield a separate continuous phase, the conductivity of the aforementioned model system at rest can serve as the conductivity of the continuous aqueous phase. For the conductivity of the lamellar phase, a value of 0.8 can be used, which is typical for most systems. In any event, the contribution of this term in the equation is often negligible.

Preferably, the viscosity of the aqueous continuous phase is less than 25 mPas, most preferably less than 15 mPas, especially less than 10 mPas, these viscosities being measured using a capillary viscometer, for example an Ostwald viscometer.

Sometimes, it is preferred for the compositions of the present invention to have solid-suspending properties (i.e. capable of suspending solid particles). Therefore, in many preferred examples, suspended solids are present. However, sometimes it may also be preferred that the compositions of the present invention do not have solid suspending properties, this is also illustrated in the examples.

In practical terms, i.e. as determining product properties, the term 'deflocculating' in respect of the polymer means that the equivalent composition, minus the polymer, has a significantly higher viscosity and/or becomes unstable. It is not intended to embrace polymers which would both increase the viscosity and not enhance the stability of the com-

position. It is also not intended to embrace polymers which would lower the viscosity simply by a dilution effect, i.e. only by adding to the volume of the continuous phase. Nor does it include those polymers which lower viscosity only by reducing the volume fraction (shrinking) of the lamellar droplets, as disclosed in our European patent application EP 301 883. Thus, although within the ambit of the present invention, relatively high levels of the deflocculating polymers can be used in those systems where a viscosity reduction is brought about, typically levels as low as from about 0.01% by weight to about 1.0% by weight can be capable of reducing the viscosity at 21 s^{-1} by up to 2 orders of magnitude.

Especially preferred embodiments of the present invention exhibit less phase separation on storage and have a lower viscosity than an equivalent composition without any of the deflocculating polymer.

Without being bound by any particular interpretation or theory, the applicants have hypothesized that the polymers exert their action on the composition by the following mechanism. The hydrophobic side-chain(s) could be incorporated only in the outer bi-layer of the droplets, leaving the hydrophilic backbone over the outside of the droplets and additionally the polymers could also be incorporated deeper inside the droplet.

When the hydrophobic side chains are only incorporated in the outer bilayer of the droplets, this has the effect of decoupling the inter- and intra-droplet forces i.e. the difference between the forces between individual surfactant molecules in adjacent layers within a particular droplet and those between surfactant molecules in adjacent droplets could become accentuated in that the forces between adjacent droplets are reduced. This will generally result in an increased stability due to less flocculation and a decrease in viscosity due to smaller forces between the droplets resulting in greater distances between adjacent droplets.

When the polymers are incorporated deeper inside the droplets also less flocculation will occur, resulting in an increase in stability. The influence of these polymers within the droplets on the viscosity is governed by two opposite effects: firstly the presence of deflocculating polymers will decrease the forces between adjacent droplets resulting in greater distances between the droplets, generally resulting in a lower viscosity of the system; secondly the forces between the layers within the droplets are equally reduced by the presence of the polymers in the droplet, this generally results in an increase in the water layer thickness, therewith increasing the lamellar volume of the droplets, therewith increasing the viscosity. The net effect of these two opposite effects may result in either a decrease or an increase in the viscosity of the product.

It is conventional in patent specifications relating to aqueous structured liquid detergents to define the stability of the composition in terms of the volume separation observed during storage for a predetermined period at a fixed temperature. In fact, this can be an over-simplistic definition of what is observed in practice. Thus, it is appropriate here to give a more detailed description.

For lamellar droplet dispersions, where the volume fraction of the lamellar phase is below 0.6 and the droplets are flocculated, instability is inevitable and is observed as a gross phase separation occurring in a relatively short time. When the volume fraction is below 0.6 but the droplets are not flocculated, the composition may be stable or unstable. When it is unstable, a phase separation occurs at a slower rate than in the flocculated case and the degree of phase separation is less.

When the volume fraction of the lamellar phase is below 0.6, whether the droplets are flocculated or not, it is possible to define stability in the conventional manner. In the context of the present invention, stability for these systems can be defined in terms of the maximum separation compatible with most manufacturing and retail requirements. That is, the 'stable' compositions will yield no more than 2% by volume phase separation as evidenced by appearance of 2 or more separate layers when stored at 25°C for 21 days from the time of preparation.

In the case of the compositions where the lamellar phase volume fraction is 0.6 or greater, it is not always easy to apply this definition. In the case of the present invention, such systems may be stable or unstable, according to whether or not the droplets are flocculated. For those that are unstable, i.e. flocculated, the degree of phase separation may be relatively small, e.g. as for the unstable non-flocculated systems with the lower volume fraction. However, in this case the phase separation will often not manifest itself by the appearance of a distinct layer of continuous phase but will appear distributed as 'cracks' throughout the product. The onset of these cracks appearing and the volume of the material they contain are almost impossible to measure to a very high degree of accuracy. However, those skilled in the art will be able to ascertain instability because the presence of a distributed separate phase greater than 2% by volume of the total composition will readily be visually identifiable by such persons. Thus, in formal terms, the above-mentioned definition of 'stable' is also applicable in these situations, but disregarding the requirement for the phase separation to appear as separate layers.

Especially preferred embodiments of the present invention yield less than 0.1% by volume visible phase separation after storage at 25°C for 90 days from the time of preparation.

It must also be realized that there can be some difficulty in determining the viscosity of an unstable liquid.

When the volume fraction of the lamellar phase is less than 0.6 and the system is deflocculated or when the volume fraction is 0.6 or greater and the system is flocculated, then phase separation occurs relatively slowly and meaningful viscosity measurement can usually be determined quite readily. For all compositions of the present invention it is usually preferred that their viscosity is not greater than 2.5 Pas, most preferably no more than 1.0 Pas, and especially not

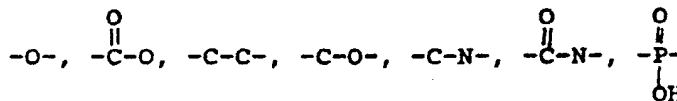
greater than 100 mPa.s. When the volume fraction of the dispersed phase is less than 10% and the droplets are flocculated, then often the rapid phase separation occurs, making it more difficult to determine the viscosity. However, it is usually possible to obtain a figure which indicates the effect of the deflocculating polymer in the compositions according to the present invention. Where this difficulty arises in the compositions exemplified hereinbelow, it is indicated accordingly.

The compositions according to the invention may contain only one, or a mixture of deflocculating polymer types. The term 'polymer types' is used because, in practice, nearly all polymer samples will have a spectrum of structures and molecular weights and often impurities. Thus, any structure of deflocculation polymers describes in this specification refers to polymers which are believed to be effective for deflocculation purposes as defined hereabove. In practice these effective polymers may constitute only part of the polymer sample, provided that the amount of deflocculation polymer in total is sufficient to effect the desired deflocculation effects. Furthermore, any structure described herein for an individual polymer type, refers to the structure of the predominating deflocculating polymer species and the molecular weight specified is the weight average molecular weight of the deflocculation polymers in the polymer mixture.

The hydrophilic backbone of the polymer generally is a linear, branched or lightly crosslinked molecular composition containing one or more types of relatively hydrophilic monomer units. Preferably the hydrophilic monomers are sufficiently water soluble to form at least a 1 % by weight solution when dissolved in water. The only limitations to the structure of the hydrophilic backbone are that the polymer must be suitable for incorporation in an active-structured aqueous liquid detergent composition and that a polymer corresponding to the hydrophilic backbone made from the backbone monomeric constituents is relatively soluble in water, in that the solubility in water at ambient temperature and at a pH of 3.0 to 12.5 is preferably more than 1 g/l, more preferred more than 5 g/l, most preferred more than 10 g/l.

Preferably the hydrophilic backbone is predominantly linear; more preferably the main chain of the backbone constitutes at least 50 % by weight, preferably more than 75 %, most preferred more than 90 % by weight of the backbone.

The hydrophilic backbone is composed of monomer units, which can be selected from a variety of units available for the preparation of polymers. The polymers can be linked by any possible chemical link, although the following types of linkages are preferred:



Examples of types of monomer units are:

(i) Unsaturated C₁₋₆ acids, ethers, alcohols, aldehydes, ketones, or esters. Preferably these monomer units are mono-unsaturated. Examples of suitable monomers are acrylic acid, methacrylic acid, maleic acid, crotonic acid, itaconic acid, aconitic acid, citraconic acid, vinyl-methyl ether, vinyl sulphonate, vinylalcohol obtained by the hydrolysis of vinyl acetate, acrolein, allyl alcohol and vinyl acetic acid.

(ii) cyclic units, either being unsaturated or comprising other groups capable of forming inter-monomer linkages. In linking these monomers the ring-structure of the monomers may either be kept intact, or the ring structure may be disrupted to form the backbone structure. Examples of cyclic monomer units are sugar units, for instance saccharides and glucosides; alkoxy units such as ethylene oxide and hydroxy propylene oxide; and maleic anhydride.

(iii) Other units, for example glycerol or other saturated polyalcohols.

Each of the above mentioned monomer units may be substituted with groups such as amino, amine, amide, sulphonate, sulphate, phosphonate, phosphate, hydroxy, carboxyl and oxide groups.

The hydrophilic backbone of the polymer is preferably composed of one or two monomer types but also possible is the use of three or more different monomer types in one hydrophilic backbone. Examples of preferred hydrophilic backbones are: homopolymers of acrylic acid, copolymers of acrylic acid and maleic acid, poly 2-hydroxy ethyl acrylate, polysaccharides, cellulose ethers, polyglycerols, polyacrylamides, polyvinylalcohol/polyvinylether copolymers, poly sodium vinyl sulphonate, poly 2-sulphato ethyl methacrylate, polyacrylamido methyl propane sulphonate and copolymers of acrylic acid and tri methyl propane triacrylate.

Optionally the hydrophilic backbone may contain small amounts of relatively hydrophobic units, e.g. those derived from polymers having a solubility of less than 1 g/l in water, provided that the overall solubility of the hydrophilic polymer backbone still satisfies the solubility requirements as specified hereabove. Examples of relatively water insoluble poly-

comonomer is selected from the group consisting of maleic anhydride, vinyl methyl ether, ethylene or styrene, and a partially esterified, neutralised co-polymer of maleic anhydride with vinyl methyl ether, ethylene or styrene.

The copolymer of the present invention is a partially esterified, neutralised copolymer of maleic anhydride with vinyl methyl ether, ethylene or styrene, and a partially esterified, neutralised co-polymer of maleic anhydride with vinyl methyl ether, ethylene or styrene, and a partially esterified, neutralised co-polymer of maleic anhydride with vinyl methyl ether, ethylene or styrene.

Insolubles are preferably less than 10% and more preferably less than 5% of the total composition. The copolymer of the present invention is a partially esterified, neutralised copolymer of maleic anhydride with vinyl methyl ether, ethylene or styrene, and a partially esterified, neutralised co-polymer of maleic anhydride with vinyl methyl ether, ethylene or styrene.

Preferably the hydrophobic moieties are selected from siloxanes, saturated and unsaturated alkyl chains, e.g. having from 5 to 24 carbon atoms, preferably from 6 to 18, most preferred from 8 to 16 carbon atoms, and are optionally bonded to the hydrophilic backbone via an alkoxy or polyalkoxy linkage, for example a polyethoxy, polypropoxy or butyloxy (or mixtures of same) linkage having from 1 to 50 alkoxy groups. Alternatively the hydrophobic side chain may be composed of relatively hydrophobic alkoxy groups, for example butylene oxide and/or propylene oxide, in the absence of alkyl or alkenyl groups. In some forms, the side-chain(s) will essentially have the character of a nonionic surfactant.

In this context it can be noted that UK patent specifications GB 1 506 427 A and GB 1 589 971 A disclose aqueous compositions including a carboxylate polymer partly esterified with nonionic surface side-chains. The compositions according to these references are hereby disclaimed from the scope of the present invention. The particular polymer described there (a partially esterified, neutralised copolymer of maleic anhydride with vinyl methyl ether, ethylene or styrene, present at from 0.1 to 2% by weight of the total composition) was not only difficult to make, but found only to work for a very narrow concentration range of five separate ingredients, said all to be essential for stability. The particular products are very alkaline (pH 12.5). In contrast, the present invention provides a broad class of readily preparable polymers, usable in a wide range of detergent lamellar droplet aqueous dispersions.

Thus, one aspect of the present invention provides a liquid detergent composition comprising a dispersion of lamellar droplets in an aqueous continuous phase, the composition having a pH less than 12.5 and yielding no more than 2% by volume phase separation when stored at 25°C for 21 days from the time of separation, and further comprising a deflocculating polymer having a hydrophilic backbone and at least one hydrophobic side-chain.

Preferably though, all compositions according to the present invention have a pH less than 11, most preferably less than 10.

US Patents 3 235 505, 3 328 309 and 3 457 176 describe the use of polymers having relatively hydrophilic backbones and relatively hydrophobic side-chains as stabilizers for emulsions. However, these products are unstable according to the definition of stability hereinbefore.

The present invention provides a liquid detergent composition which yields no more than 2% by volume phase separation when stored at 25°C for 21 days from the time of preparation and comprises a dispersion of lamellar droplets in an aqueous continuous phase and also comprises a deflocculating polymer having a hydrophilic backbone and at least one hydrophobic side-chain, with the proviso that when the composition comprises from 3% to 12% of a potassium alkyl benzene sulphonate, from 2% to 8% of a potassium fatty acid soap, from 0.5 to 5% of a nonionic surfactant, from 1 to 25% of alkalimetal tripolyphosphate, wherein the alkalimetal is sodium or potassium, and at least 50% by weight of the alkalimetal tripolyphosphate is sodium tripolyphosphate, optionally 20-65% of the sodium tripolyphosphate being replaced by tetrapotassium pyrophosphate, and from 0.1 to 2% of a partially esterified, neutralised co-polymer of maleic anhydride with vinylmethyl ether, ethylene or styrene, all percentages being by weight, the weight ratio of said sulphonate to said soap being from 1:2 to 6:1, the weight ratio of said sulphonate to said nonionic surfactant being from 3:5 to 25:1, the total amount of said sulphonate, soap and nonionic surfactant being from 7.5 to 20% by weight,

then the decoupling polymer does not consist solely of from 0.1 to 2% by weight of a partially esterified, neutralised co-polymer of maleic anhydride with vinylmethyl ether, ethylene or styrene,

and with the further proviso that

when the composition comprises soap, tetrapotassium pyrophosphate and zwitterionic surfactant,

then the decoupling polymer does not consist solely of an interpolymer of methyl ether vinyl and maleic anhydride esterified with the zwitterionic surfactant.

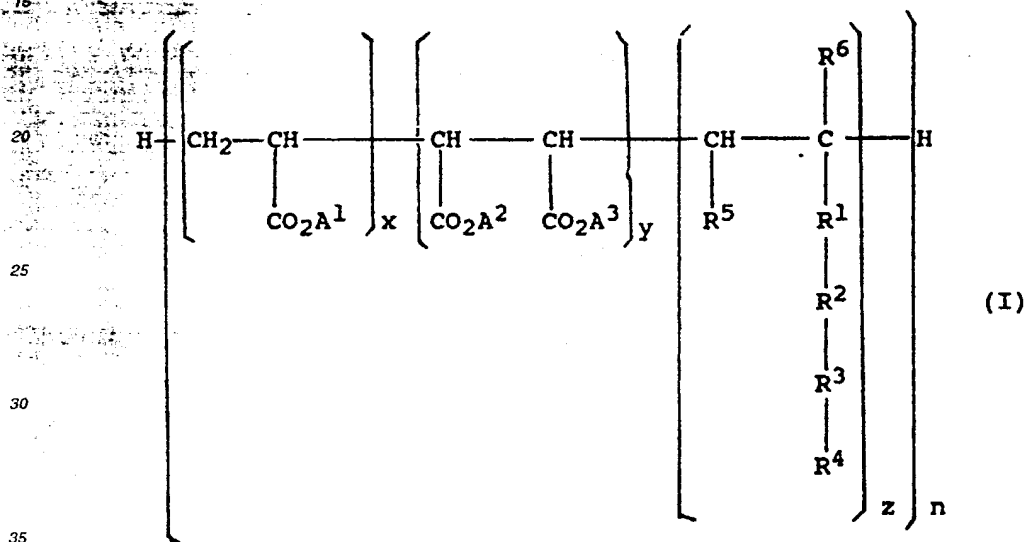
Preferably, the deflocculating polymer has a lower specific viscosity than those disclosed in GB 1 506 427 A and GB 1 589 971 A, i.e. a specific viscosity less than 0.1 measured as 1g in 100 ml of methylethylketone at 25°C. Specific viscosity is a dimensionless viscosity-related property which is independent of shear rate and is well known in the art of polymer science.

Some polymers having a hydrophilic backbone and hydrophobic side-chains are known for thickening isotropic

These polymers, however, are not of the Equimolar Ternary Specialized Type A. However, there is no evidence that polymers of this general type are usable as stabilizers and/or viscosity-reducing agents in emulsifier droplet dispersions.

Of course, in the present invention, it is possible to use delocalizing polymers wherein the backbone of the polymers is of anionic, cationic, nonionic, zwitterionic or amphoteric nature. Possibly the polymer backbones have a structure generally corresponding to a surfactant structure, and independently of whether or not the backbone has a functional group, the side-chain(s) may also have structures generally corresponding to anionic, cationic, zwitterionic or amphoteric surfactants. The only restriction is that the side-chain(s) should have hydrophobic character, relative to the polymer backbone. However, the choice of overall polymer types will usually be limited by the surfactants in the composition. For example, polymers with any cationic surfactant structural features would be less preferred in combination with anionic surfactants, and vice versa.

One preferred class of polymers for use in the compositions of the present invention comprises those of general formula (I):



wherein:

z is 1, (x + y) · z is from 4 : 1 to 1,000 : 1, preferably from 6 : 1 to 250 : 1; in which the monomer units may be in random order; y preferably being from 0 up to a maximum equal to the value of x; and n is at least 1;

R¹ represents -CO-O-, -O-, -O-CO-, -CH₂-, -CO-NH- or is absent:

R² represents from 1 to 50 independently selected alkyleneoxy groups preferably ethylene oxide or propylene oxide groups, or is absent, provided that when R³ is absent and R⁴ represents hydrogen or contains no more than 4 carbon atoms, then R² must contain an alkyleneoxy group with at least 3 carbon atoms;

R³ represents a phenylene linkage, or is absent;

R⁴ represents hydrogen or a C₁₋₂₄ alkyl or C₂₋₂₄ alkenyl group, with the provisos that

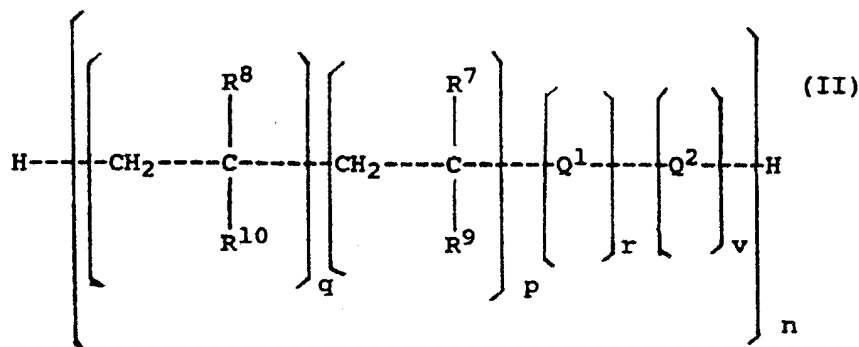
a) when R¹ represents -O-CO-. R² and R³ must be absent and R⁴ must contain at least 5 carbon atoms,
b) when R² is absent, R⁴ is not hydrogen and when R³ is absent, then R⁴ must contain at least 5 carbon atoms;

R⁵ represents hydrogen or a group of formula -COOA⁴:

R^6 represents hydrogen or C_{1-4} alkyl, and

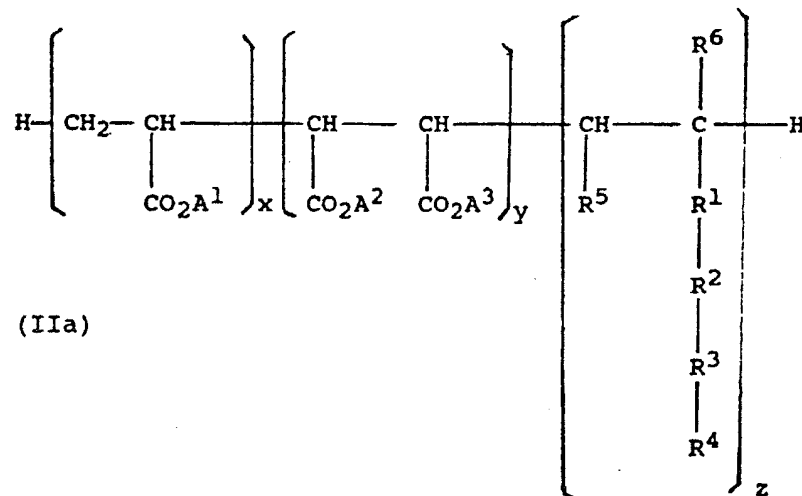
A^1 , A^2 , A^3 and A^4 are independently selected from hydrogen, alkali metals, alkaline earth metals, ammonium and amine bases and C_{1-4} alkyl.

Another class of polymers for use in compositions of the present invention comprise those of formula (II)



wherein:

Q^2 is a molecular entity of formula (IIa):



wherein z and R^{1-6} are as defined for formula (I); A^{1-4} are as defined for formula (I) or $(\text{C}_2\text{H}_4\text{O})_t\text{H}$, wherein t is from 1-50, and wherein the monomer units may be in random order;

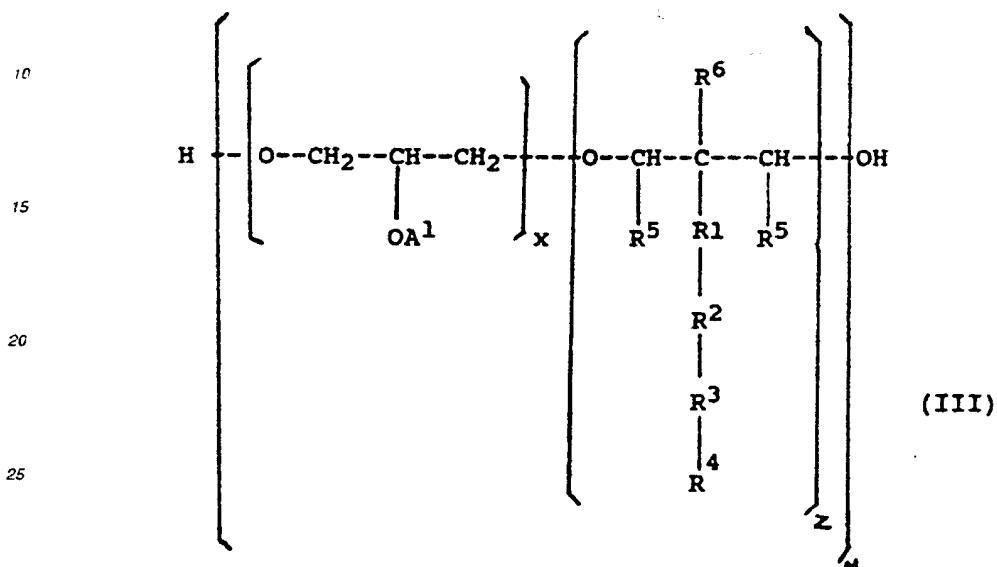
Q^1 is a multifunctional monomer, allowing the branching of the polymer, wherein the monomers of the polymer may be connected to Q^1 in any direction, in any order, therewith possibly resulting in a branched polymer. Preferably Q^1 is trimethyl propane triacrylate (TMPTA), methylene bisacrylamide or divinyl glycol.

n and z are as defined above; v is 1; and $(x + y + p + q + r) : z$ is from 4 : 1 to 1,000 : 1, preferably from 6 : 1 to 250 : 1; in which the monomer units may be in random order, and preferably either p and q are zero, or r is zero;

R^7 and R^8 represent $-\text{CH}_3$ or $-\text{H}$;

R⁹ and R¹⁰ represent substituent groups such as amino, amine, amide, sulphonate, sulphate, phosphonate, phosphate, hydroxy, carboxyl and oxide groups, preferably they are selected from -SO₃Na, -CO-O-C₂H₄-OSO₃Na, -CO-O-NH-C(CH₃)₂-SO₃Na, -CO-NH₂, -O-CO-CH₃, -OH.

A third class of polymers for use in compositions of the present invention comprise those of formula (III)



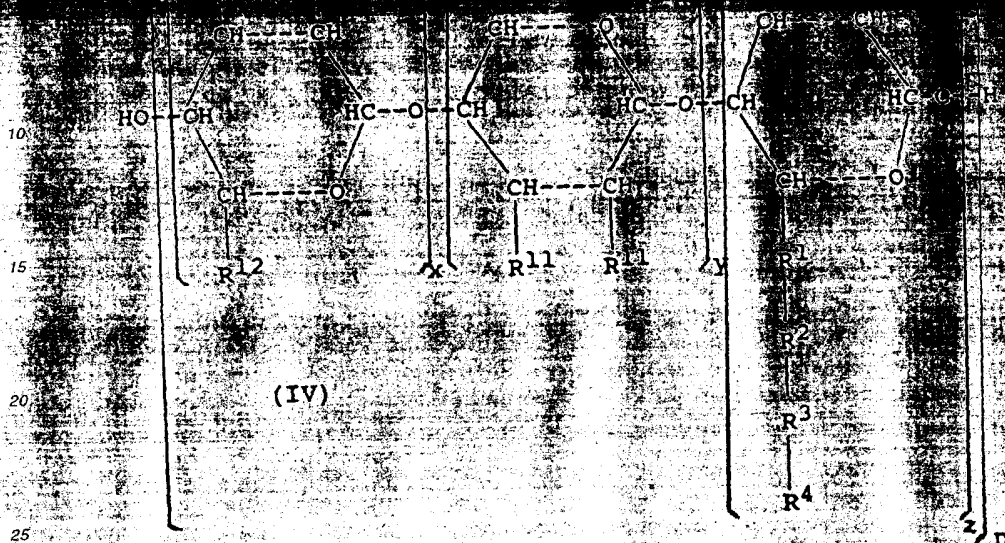
30 wherein:

x is from 4 to 1,000, preferably from 6 to 250; n is 1, z and R¹⁻⁶ are as defined in formula I, wherein the monomers units may be in random order;

35 A¹ is as defined above for formula I, or -CO-CH₂-C(OH)CO₂A¹-CH₂-CO₂A¹, or may be a branching point whereto other molecules of formula (III) are attached

Examples of molecules of this formula are hydrophobically modified polyglycerol ethers or hydrophobically modified condensation polymers of polyglycerol and citric acid anhydride.

Other suitable materials have the formula (IV)



Wherein

30 z , n and A^1 are as defined for formula I, $(x+y) : z$ is from 4 : 1 to 1,000 : 1, preferably from 6 : 1 to 250 : 1, wherein the monomer units may be in random order.

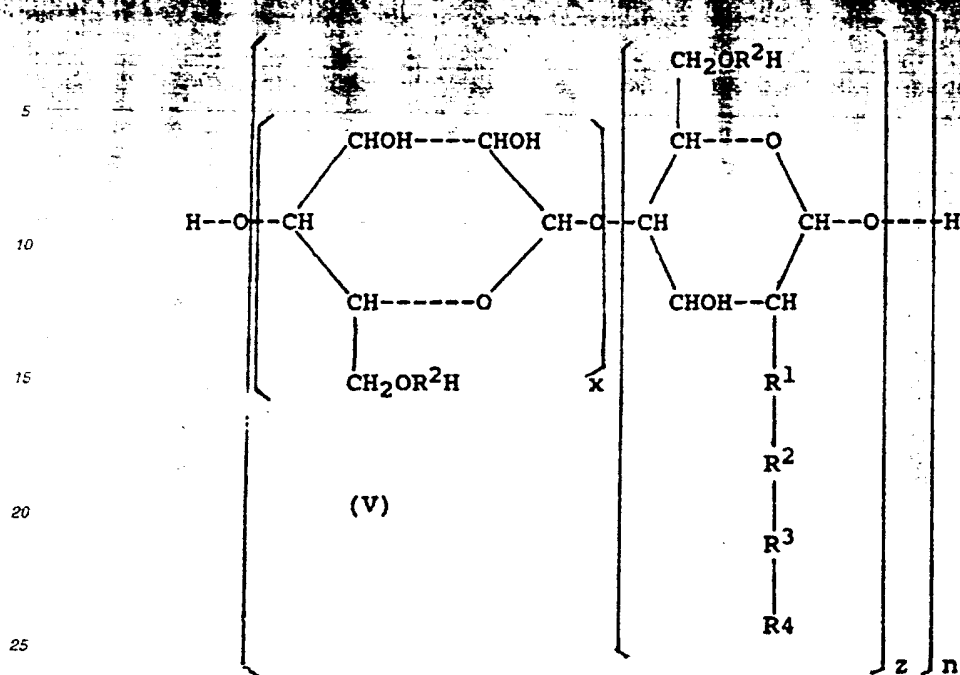
R^1 is as defined above for formula I, or can be $-\text{CH}_2-\text{O}-$, $-\text{CH}_2-\text{O}-\text{CO}-$, $-\text{NH}-\text{CO}-$;

35 R^{2-4} are as defined in formula I;

R^{11} represents $-\text{OH}$, $-\text{NH}-\text{CO}-\text{CH}_3$, $-\text{SO}_3\text{A}^1$ or $-\text{OSO}_3\text{A}^1$;

40 R^{12} represents $-\text{OH}$, $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OSO}_3\text{A}^1$, COOA^1 , $-\text{CH}_2-\text{OCH}_3$.

Examples of molecules of this formula are hydrophobically modified polydextran, -dextran sulphonates, and -dextran sulphates and the commercially available lipoheteropolysaccharides Emulsan or Biosan LP-31 (ex Petroferm). Other suitable polymer materials have the following formula (V):

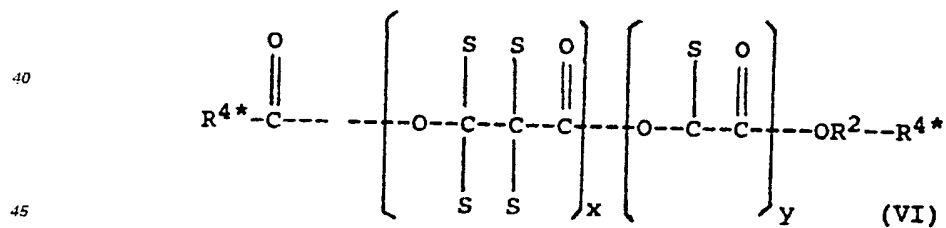


Wherein:

z, n and R^{1-6} are as defined above for formula I; and x is as defined for formula III;

Similar materials are disclosed in GB-A-2,043,646.

Other suitable polymers are hydrophobically modified condensation polymers of -hydroxy acids of formula (VI):



wherein:

If z is the total of R^4 groups, then the ratio $(x + y) : z$ is from 4 : 1 to 1,000 : 1, preferably from 6 : 1 to 250 : 1; R^4 is R^4 or -H;

R^2 and R^4 are as defined above for formula I,

and S is selected from -H, -COOA¹, -CH₂COOA¹, -CH(COOA¹)₂, (-CH₂COOA¹)₂H, wherein A¹ is as defined for formula I or is R^4 ;

with the proviso that at least one R^4 group is present as a side chain;



$x, z: S$ and R^4 are as defined above for formula VI

v is 0 or 1

The salts of the polymers of the above formulas may be formed with any organic or inorganic cation defined for A^1-A^4 and which is capable of forming a water-soluble salt with a low molecular weight carboxylic acid. Preferred are the alkali metal salts, especially of sodium or potassium.

One preferred sub-class comprises those polymers which contain substantially no maleic acid (or esterified form thereof) monomer units.

As already referred to above, only polymers of which the value of n is equal to or more than 1 are believed to be effective as deflocculating polymers. In practice however generally a mixture of polymers will be used. For the purpose of the present invention it is not necessary that the polymer mixtures as used have an average value of n which is equal or more than one; also polymer mixtures of lower average n value may be used, provided that an effective amount of the polymer molecules have one or more n -groups. Dependant on the type and amount of polymer used, the amount of effective polymer as calculated on the basis of the total polymer fraction may be relatively low, for example samples having an average n -value of about 0.1 have been found to be effective as deflocculation polymers.

When the sample and standards are of the same chemical composition, the approximate true molecular weight of the sample can be calculated, but if such standards are not available, it is common practice to use some other well characterized standards as a reference. The molecular weight obtained by such means is not the absolute value, but is useful for comparative purposes. Sometimes it will be less than that resulting from a theoretical calculation for a dimer.

It is possible that when the same sample is measured, relative to different sets of standards, different molecular weights can be obtained. We have found this to be the case when using, say, polyethylene glycol, polyacrylate and polystyrene sulphonate standards. For the compositions of the present invention exemplified hereinbelow, the molec-

molar weights specified by reference to the above formulae.

For the polymers of formula (I to VII) and their salts, it is preferred to have a weight average molecular weight in the region of from 500 to 500,000, preferably from 750 to 100,000, most preferably from 1,000 to 30,000, especially from 2,000 to 10,000 when measured by GPC using polystyrene standards. For the purposes of this definition, the molecular weights of the standards are measured by the absolute intrinsic viscosity method described by Noda, Tsuge and Nagasawa in Journal of Physical Chemistry, Volume 74, (1970), pages 710-719.

As well as the polymers of the above formulas and their salts, many other suitable polymers are known, although previously not for inclusion in lamellar dispersions of surfactant. Such known polymers are described, for example, in R. Buscall and T. Comer, Colloids and Surfaces, 17 (1986) 25-38; Buscall and Comer, *ibid.*, pp. 39-49, European Patent Applications EP-A-57 875 and EP-A-99 179, US Patent 4 559 159 and UK Patent GB 1 052 924. These references also disclose methods for making the polymers therein described and which, by analogy those skilled in the art will be capable of adapting for preparing other polymers for use in the present invention. The polymers may also be made by methods generally analogous to any of those described in any of patent documents EP-A-244 066, US-A-3 235 505, US-A-3 328 309 and US-A-3 457 176 referred to hereinbefore.

Most preferably, however, we have found that the polymers for use in the compositions of the present invention can be efficiently prepared using conventional aqueous polymerization procedures, but employing a process wherein the polymerization is carried out in the presence of a suitable cosolvent and wherein the ratio of water to co-solvent is carefully monitored so as to maintain the ratio of water to cosolvent equal or greater than unity during the reaction, thereby keeping the polymer, as it forms, in a sufficiently mobile condition and to prevent unwanted homopolymerization and precipitation of the polymer from the hydrophobic monomer.

A preferred process for preparing the polymers provides a product in unique form as a relatively high solids, low viscosity, opaque or semi-opaque product intermediate between a true clear or limpid solution, and an emulsion consisting entirely of non-agglomerated particles. The product exhibits no gelling, coagulation or product separation on standing for at least two weeks. It is further preferably characterized in that upon dilution in water to 0.25 % by weight, the turbidity of the resultant preparation is at least 10 Nephelometric Turbidity Units (N.T.U.'s).

This preferred process is especially suited to preparation of the polymers and salts according to formula (I and II) as hereinbefore defined. The particular cosolvent chosen for the reaction will vary depending upon the particular monomers to be polymerized. The co-solvent selected should be miscible with water, dissolve at least one of the monomers, but not react with the monomers or with the polymer as it is produced and be substantially readily removed by simple distillation or azeotropic distillation procedures.

The particular co-solvent chosen for the reaction will vary depending upon the particular monomers to be polymerized. The cosolvent selected should be miscible with water, dissolve at least one of the monomers, but not react with the monomers or with the polymers as it is produced and be substantially readily removed by simple distillation or azeotropic distillation procedures. Suitable co-solvents include isopropanol, n-propanol, acetone, lower (C_1 to C_4) alcohols, ketones and esters. Isopropanol and normal propanol are the most preferred.

The ratio of water to co-solvent is preferably carefully regulated. If too low an amount of co-solvent is employed, precipitation of hydrophobic monomer or homopolymer may occur; too high a co-solvent level is more expensive and time-consuming to remove, results in too high product viscosity and, in some cases, may cause precipitation of the water-soluble polymer.

In some case it is critical that the ration of water to cosolvent is equal or greater than unity during the reaction.

The polymerization is carried out in the presence of free-radical initiators. Examples of water-soluble, free-radical initiators which are suitable for the polymerization are the usual thermal decomposition initiators such as hydrogen peroxide, peroxydisulphates, especially sodium peroxydisulphate or ammonium peroxydisulphate, or azo-bis(2-aminopropane) hydrochloride. Redox initiators such as tertiary butyl hydroperoxide/bisulphite; tertiary butyl hydroperoxide/sodium formaldehyde sulphonylate; or hydrogen peroxide with a ferrous compound can also be used.

Preferably, from 0.1 to 5% by weight, based on the sum of the monomers, of the initiators is present in the mixture. The polymerization takes place in an aqueous co-solvent medium, and the concentration is advantageously chosen so that the aqueous co-solvent solution contains from 10 to 55, preferably from 20 to 40% by weight of total monomers. The reaction temperature can vary within wide limits, but is advantageously chosen to be from 60° to 150°C, preferably from 70° to 95°C. If the reaction is carried out at above the boiling point of water, a pressure-tight vessel, such as an autoclave, is chosen as the reaction vessel.

Furthermore, the regulators conventionally used for free-radical polymerization in an aqueous medium, e.g. thioglycolic acid or C_1 to C_4 aldehydes, or branching agents, such as methylene bisacrylamide or divinyl glycol or TMPTA, can be employed, the amounts being from 0.1 to 10% by weight preferably from 0.5 to 5% by weight, respectively, and the percentages being based on the total amount of the monomers.

The turbidity of the prepared polymers may be measured using a Hach Model 2100A Turbidimeter. It was found that direct measurement on the polymers was not possible, and that useful readings could only be made when the polymers were diluted to 0.25 % by weight solid contents with deionized water.

suspended particles of solid, because the interfacial energy of the liquid is higher than the solubility limit of the electrolyte. Mixtures of detergents may also be used, with one or more of the electrolytes being in the dissolved aqueous phase and one or more being substantially only in the suspended solid phase. Two or more electrolytes may also be distributed approximately proportionally between these two phases. In fact, this may depend on processing, e.g. the order of addition of components. On the other hand, the term salts includes all organic and inorganic materials which may be included, other than surfactants and water. Whether or not they are ionic, and this term encompasses the sub-set of the electrolytes, water-soluble materials.

The only restriction on the total amount of detergent-active material and electrolyte (if any) is that in the compositions of the invention, together, they must result in formation of an aqueous lamellar dispersion. Thus, within the ambit of the present invention, a very wide variation in surfactant types and levels is possible. The selection of surfactant types and their proportions in order to obtain a stable liquid with the required structure will be fully within the capability of those skilled in the art. However, it can be mentioned that an important sub-class of useful compositions is those where the detergent-active material comprises blends of different surfactant types. Typical blends useful for fabric washing compositions include those where the primary surfactant(s) comprise nonionic and/or a non-alkoxylated anionic and/or an alkoxylated anionic surfactant.

In many (but not all) cases, the total detergent-active material may be present at from 2% to 60% by weight of the total composition, for example from 5% to 40% and typically from 10% to 30% by weight. However, one preferred class of compositions comprises at least 20%, most preferably at least 25%, and especially at least 30% of detergent-active material based on the weight of the total composition.

In the case of blends of surfactants, the precise proportions of each component which will result in such stability and viscosity will depend on the type(s) and amount(s) of the electrolytes, as is the case with conventional structured liquids.

In the widest definition the detergent-active material in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, sub-classes and specific materials described in 'Surface Active Agents' Vol. I, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' Vol. II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of 'McCutcheon's Emulsifiers & Detergents' published by the McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch', H. Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

Suitable nonionic surfactants include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide, either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6 - C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulfoxides.

Suitable anionic surfactants are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8 - C_{18}) alcohols produced, for example, from tallow or coconut oil, sodium and potassium alkyl (C_9 - C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10} - C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_8 - C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8 - C_{20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolyzing with a base to produce a random sulphonate, and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10} - C_{20} alpha-olefins, with SO_3 and then neutralizing and hydrolyzing the reaction product. The preferred anionic detergent compounds are sodium (C_{11} - C_{15}) alkyl benzene sulphonates and sodium (C_{16} - C_{18}) alkyl sulphates.

Also possible is that part or all of the detergent active material is an stabilising surfactant, which has an average alkyl chain length greater than 6 C-atoms, and which has a salting out resistance, greater than, or equal to 6.4. These stabilising surfactants are disclosed in our co-pending European patent application EP 0328177, published 16.08.89. Examples of these materials are alkyl polyalkoxylated phosphates, alkyl polyalkoxylated sulposuccinates;

polysaccharides and mixtures thereof.

It is also preferred, to include an alkali metal soap of a long chain mono- or dicarboxylic acid having from 12 to 18 carbon atoms. Typical acids of this kind are oleic acid, ricinoleic acid, and lauric acid. Other suitable oils are castor oil, rapeseed oil, groundnut oil, coconut oil, palmkernel oil or mixtures thereof. The number of potassium soaps of these acids can be used.

Preferably the amount of water in the composition is from 5 to 95%, more preferred from 25 to 75%, most preferred from 30 to 50%. Especially preferred less than 45% by weight.

The compositions optionally also contain electrolyte in an amount sufficient to bring about structuring of the detergent active material. Preferably though, the compositions contain from 1% to 60%, especially from 10 to 45% of a salting-out electrolyte. Salting-out electrolyte has the meaning ascribed to in specification EP-A-79 646. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included, provided if of a kind and in an amount compatible with the other components and the composition is still in accordance with the definition of the invention claimed herein. Some or all of the electrolyte (whether salting-in or salting-out), or any substantially water-insoluble salt which may be present, may have detergency builder properties. In any event, it is preferred that compositions according to the present invention include detergency builder material, some or all of which may be electrolyte. The builder material is any capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the composition with other beneficial properties such as the generation of an alkaline pH, the suspension of soil removed from the fabric and the dispersion of the fabric softening clay material.

Examples of phosphorous-containing inorganic detergency builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates. Phosphonate sequestrant builders may also be used.

Examples of non-phosphorus-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

In the context of inorganic builders, we prefer to include electrolytes which promote the solubility of other electrolytes, for example use of potassium salts to promote the solubility of sodium salts. Thereby, the amount of dissolved electrolyte can be increased considerably (crystal dissolution) as described in UK patent specification GB 1 302 543.

Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates, carboxymethyloxysuccinates, carboxymethyloxymalonates, ethylene diamine-N,N, disuccinic acid salts, polyepoxysuccinates, oxydiacetates, triethylene tetramine hexacetic acid salts, N-alkyl imino diacetates or dipropionates, alpha sulpho- fatty acid salts, dipicolinic acid salts, oxidised polysaccharides, polyhydroxysulphonates and mixtures thereof.

Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid, tartrate mono succinate and tartrate di succinate.

In the context of organic builders, it is also desirable to incorporate polymers which are only partly dissolved in the aqueous continuous phase. This allows a viscosity reduction (owing to the polymer which is dissolved) whilst incorporating a sufficiently high amount to achieve a secondary benefit, especially building, because the part which is not dissolved does not bring about the instability that would occur if substantially all were dissolved.

Examples of partly dissolved polymers include many of the polymer and co-polymers salts already known as detergency builders. For example, may be used (including building and non-building polymers) polyethylene glycols, polyacrylates, polymaleates, polysugars, polysugarsulphonates and co-polymers of any of these. Preferably, the partly dissolved polymer comprises a co-polymer which includes an alkali metal salt of a polyacrylic, polymethacrylic or maleic acid or anhydride. Preferably, compositions with these co-polymers have a pH of above 8.0. In general, the amount of viscosity-reducing polymer can vary widely according to the formulation of the rest of the composition. However, typical amounts are from 0.5 to 4.5% by weight.

It is further possible to include in the compositions of the present invention, alternatively, or in addition to the partly dissolved polymer, yet another polymer which is substantially totally soluble in the aqueous phase and has an electrolyte resistance of more than 5 grams sodium nitrilotriacetate in 100 ml of a 5% by weight aqueous solution of the polymer, said second polymer also having a vapour pressure in 20% aqueous solution, equal to or less than the vapour pressure of a reference 2% by weight or greater aqueous solution of polyethylene glycol having an average molecular weight of 6,000, said second polymer having a molecular weight of at least 1,000.

The incorporation of the soluble polymer permits formulation with improved stability at the same viscosity (relative to the composition without the soluble polymer) or lower viscosity with the same stability. The soluble polymer can also reduce viscosity drift, even when it also brings about a viscosity reduction. Here, improved stability and lower viscosity mean over and above any such effects brought about by the deflocculating polymer.

It is usually preferable to incorporate the soluble polymer with a partly dissolved polymer which has a large insoluble component, that is because although the building capacity of the partly dissolved polymer will be good (since relatively high quantities can be stably incorporated), the viscosity reduction will not be optimum (since little will be dissolved). Thus, the soluble polymer can usefully function to reduce the viscosity further, to an ideal level.

The soluble polymer can, for example, be incorporated at from 0.05 to 20% by weight, although usually, from 0.1 to 10% by weight of the total composition is sufficient, and especially from 0.2 to 3.5-4.5% by weight. It has been found that the presence of deflocculating polymer increase the tolerance for higher levels of soluble polymer without stability problems. A large number of different polymers may be used as such a soluble polymer, provided the electrolyte resistance and vapour pressure requirements are met. The former is measured as the amount of sodium nitrilotriacetate (NaNTA) solution necessary to reach the cloud point of 100 ml of a 5% solution of the polymer in water at 25°C, with the system adjusted to neutral pH, i.e. about 7. This is preferably effected using sodium hydroxide. Most preferably, the electrolyte resistance is 10 g NaNTA, especially 15 g. The latter indicates a vapour pressure low enough to have sufficient water binding capability, as generally explained in the Applicants' specification GB-A-2 053 249. Preferably, the measurement is effected with a reference solution at 10% by weight aqueous concentration, especially 18%.

Typical classes of polymers which may be used as the soluble polymer, provided they meet the above requirements, include polyethylene glycols, Dextran, Dextran sulphonates, polyacrylates and polyacrylate/maleic acid co-polymers.

The soluble polymer must have an average molecular weight of at least 1,000 but a minimum average molecular weight of 2,000 is preferred.

The use of partly soluble and the use of soluble polymers as referred to above in detergent compositions is described in our copending European patent applications EP 301 882 and EP 301 883.

Although it is possible to incorporate minor amounts of hydrotropes such as lower alcohols (e.g. ethanol) or alkanolamines (e.g. triethanolamine), in order to ensure integrity of the lamellar dispersion we prefer that the compositions of the present invention are substantially free from hydrotropes. By hydrotrope is meant any water soluble agent which tends to enhance the solubility of surfactants in aqueous solution.

Apart from the ingredients already mentioned, a number of optional ingredients may also be present, for example lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, fabric softeners such as clays, amines and amine oxides, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases, amylases and lipases (including Lipolase® (Trade Mark) ex Novo), germicides and colourants.

Amongst these optional ingredients, as mentioned previously, are agents to which lamellar dispersions without deflocculating polymer are highly stability-sensitive and by virtue of the present invention, can be incorporated in higher, more useful amounts. These agents cause a problem in the absence of deflocculating polymer because they tend to promote flocculation of the lamellar droplets. Examples of such agents are soluble polymers, soluble builder such as succinate builders, fluorescers like Blankophor RKH®, Tinopal® LMS, and Tinopal® DMS-X and Blankophor BBH® as well as metal chelating agents, especially of the phosphonate type, for example the Dequest® range sold by Monsanto.

The invention will now be illustrated by way of the following Examples. In all Examples, unless stated to the contrary, all percentages are by weight.

A. BASE COMPOSITIONS

Table 1a

Composition of basic formulations i.e. without deflocculating polymer.					
Ingredient	Basic formulation (% w/w)				
	1	2	3	4	5
NaDoBS	28.0	24.5	19.7	26.7	26.1
Synperonic A7	6.5	9.9	7.9	10.7	10.5
Na Citrate	16.4	16.4	11.0	9.0	10.9
Water	49.0	49.2	61.4	53.6	52.5

Table 1a (continued)

Composition of basic formulations i.e. without deflocculating polymer.					
Ingredient	Basic formulation (% w/w)				
	1	2	3	4	5
Deflocculating polymer	weights additional to basic formulation				

Table 1b

Composition of basic formulations					
Ingredient	Basic formulation (% w/w)				
	6	7	8	9	10
NaDoBS	25.6	25.0	12.9	12.6	12.3
Synperonic A7	10.3	10.0	5.2	5.1	5.0
Na Citrate	12.8	14.7	12.9	14.8	16.5
Water	51.3	50.3	69.0	67.5	66.2
Deflocculating polymer	weights additional to basic formulation				

Table 1c

Composition of basic formulations.	
Ingredient	Basic formulation (% w/w)
	11
Na DoBS	23.5
Synperonic A7	9.5
Na Citrate	19.7
Water	47.3
Deflocculating polymer	weights additional to basic formulation
Ingredient	Basic formulation (% w/w)
	12
Na DoBS	17.1
Dobanol 23-6.5	7.0
TrEA	2.0
Na-citrate	20.0
Deflocculating polymer	if any
Water	up to 100

Table 1d

Composition of basic formulations								
Ingredient	Basic formulation (% w/w)							
	13	14	15	16	17	18	19	20
Na DoBS	8.5	8.5	8.5	8.5	7.5	7.5	6.4	4.3
Synperonic A7	2.0	2.0	2.0	2.0	3.0	3.0	4.0	6.0
Na Oleate	2.7	5.4	8.1	10.8	8.1	10.8	-	-

EP 0 346 995 B1

Table 1d (continued)

Composition of basic formulations								
Ingredient	Basic formulation (% w/w)							
	13	14	15	16	17	18	19	20
Glycerol	----- 5.0 -----							
Borax	----- 3.5 -----							
STP	----- 22 -----							
Deflocculating Polymer	----- if any -----							
Water	----- up to 100 -----							

Table 1e

Composition of basic formulations.					
Ingredient	Basic formulation (% w/w)				
	21	22	23	24	25
Na DoBS	9.6	9.9	10.1	10.2	10.4
Na Oleate	16.2	16.6	16.9	17.2	17.6
Synperonic A7	6.0	5.3	4.8	4.4	4.0
Glycerol	5.0				
Borax	3.5				
STP	15				
Deflocculating polymer	if any				
Water	up to 100				

Table 1f

Composition of Basic formulations					
Ingredient	Basic formulation (% w/w)				
	26	27	28/31	29/32	30/33
Na DoBS	10.2	9.6	20.6	21.5	21.8
Na Oleate	16.9	15.9	-	-	-
Synperonic A7	4.8	4.5	4.4	3.5	3.2
Glycerol	5.0	5.0	5.0	5.0	5.0
Borax	3.5	3.5	3.5	3.5	3.5
STP	15.0	15.0	22.0	22.0	22.0
Silicone oil/DB 100	0.25	0.25	0.25	0.25	0.25
Gasil 200®	2.0	2.0	2.0	2.0	2.0
Na SCMC	0.1	0.1	0.3	0.3	0.3
Tinopal® CBS-X	0.1	0.1	0.1	0.1	0.1
Blancophor RKH 766®	-	-	0/0.2	0/0.2	0/0.2
Dequest 2060S®	-	-	0.4	0.4	0.4
Perfume	0.3	0.3	0.3	0.3	0.3
Alcalase 2.5l	0.5	0.5	0.5	0.5	0.5
Deflocculating polymer	if any				
Water	up to 100				

Table 1g

Composition of basic formulations		
Ingredient	Basic formulation (% w/w)	
	34	35
Na DoBS	9.8	12.3
Synperonic A7	2.3	2.9
Glycerol	5.0	6.3
Borax	3.5	4.4
STP	25.0	31.3
Water	54.4	42.8
Deflocculating polymer	weights additional to basic formulation	

Table 1h

Composition of basic formulations.

Ingredients	Basic formulation (% w/w)				
	36	37	38	39	40
NaDoBS	<.....21.5.....>				
Synperonic A7	<.....3.5.....>				
Glycerol	<.....5.0.....>				
Borax	<.....3.5.....>				
KTP	0	2	4	6	8
STP	22	20	18	16	14
Silicon oil	<.....0.25.....>				
Gasil 200	<.....2.0.....>				
Na SCMC	<.....0.3.....>				
Tinopal CBS-X	<.....0.1.....>				
Dequest 2060S (as 100%)	<.....0.4.....>				
Perfume	<.....0.3.....>				
Alcalase 2.5L	<.....0.5.....>				
Deflocculating polymer	<.....0.75.....>				
Water	<.....39.9.....>				

EP 0 346 995 B1

Table 1i

Composition of basic formulations					
Ingredients	Basic formulation (% w/w)				
	41	42	43	44	45
NaDoBS	9.6	9.4	9.2	8.9	8.3
Na-Oleate	15.9	15.6	15.3	14.7	13.7
Synperonic A7	4.5	4.4	4.3	4.2	3.9
Glycerol	5.0	4.9	4.8	4.6	4.3
Borax	3.5	3.4	3.4	3.2	3.0
KTP	-	2.0	3.8	7.4	13.8
STP	15.0	14.7	14.4	13.9	12.9
Silicon oil	0.25	0.25	0.24	0.23	0.22
Gasil 200	2.0	2.0	1.9	1.9	1.7
Na-SCMC	0.1	0.1	0.1	0.1	0.1
Tinopal CBS-X	0.1	0.1	0.1	0.1	0.1
Perfume	0.3	0.3	0.3	0.27	0.26
Alcalase 2.5L	0.5	0.5	0.5	0.46	0.43
Deflocculating polymer	0.75	0.74	0.72	0.69	0.65
Water	42.5	41.6	40.9	39.4	36.6

Table 1k

Composition of basic formulations			
Ingredient	Basic formulation (%w/w)		
	46	47	48
NaDoBS	27.1	31.5	33.9
Synperonic A7	11.5	13.4	14.5
Na Citrate	15.3	13.8	12.9
Water	46.1	41.3	38.7
Deflocculating polymer	Weights additional to basic formulations		

Table 1l

Composition of basic formulations							
Ingredient	Basic formulation (%w/w)						
	49	50	51	52	53	54	55
NaLAS	6.2	-	-	-	6.3	5.2	-
K LAS	-	6.5	6.5	6.3	-	-	6.3
NaOleate	8.8	-	-	-	-	-	-
K Laurate	-	-	3.8	-	3.8	3.2	-
K Oleate	-	9.4	5.5	9.2	5.5	4.6	9.2
Synperonic A7	10.0	3.5	10.0	10.0	10.0	8.4	-
Synperonic A3	-	-	-	-	-	-	10.0
Glycerol	5.0	5.0	5.0	5.0	5.0	3.64	3.64
Borax	3.5	3.5	3.5	-	-	-	-
Boric-acid	-	-	-	2.28	2.28	1.66	1.66
KOH	-	-	-	1.0	1.0	0.75	0.75
KTP	7.0	-	-	-	-	-	-

EP 0 346 995 B1

Table 1m (continued)

Composition of basic formulations			
Ingredient	Basic formulation (%w/w)		
	61	62	63
Boric-acid	-	-	2.28
KOH	-	-	2.2
NaOH	1.0	-	-
Borax	5.8	2.0	-
Na-citrate	-	5.0	-
Citric-acid	1.5	-	1.50
Zeolite A4	25.3	30.0	20.0
NaCMC	-	0.3	0.3
Tinopal CBS-X	-	0.13	0.1
Silicon DB100	-	-	0.25
Dequest 2060S (as 100%)	-	-	0.4
Perfume	-	0.22	0.3
Alcalase 2.34L	-	0.5	0.5
Deflocculating polymer (if any)	0/0.5	0/0.5	0/0.5
Water	up to 100		
pH	8.8	9.1	7.7

Table 1p

Composition of basic formulations							
Ingredient	Basic formulation (%w/w)						
	64	65	66	67	68	69	70
Na Dobs	14.4	10.3	6.2	11.0	13.6	12.3	12.3
Synperonic A7	11.6	19.3	27.0	13.8	17.0	15.4	15.4
Na Oleate	8.7	6.2	3.7	6.7	8.2	7.5	7.5
Na Laurate	5.9	4.3	2.6	4.6	5.7	5.1	5.1
Na ₂ CO ₃	4.0	4.0	4.0	4.0	4.0	2.0	6.0
Glycerol	5.0						
Borax	3.5						
Dequest 2066 (as 100%)	0.4						
Silicon DB100	0.1						
Savinase	0.3						
Amylase	0.1						
Tinopal CBS-X	0.1						
Perfume	0.3						
Deflocculating polymer (if any)	0/1.0						
Water	up to 100						
pH	9.7-10.0						

Table 1q

Composition of basic formula							
Ingredient	Basic formulation (%w/w)						
	71	72	73	74	75	76	77
Na Dobs	14.4	10.3	11.0	12.3	13.6	12.3	12.3
Synperonic A7	11.6	19.3	13.8	15.4	17.0	15.4	15.4
Na Oleate	8.7	6.2	6.7	7.5	8.2	7.5	7.5
Na Laurate	5.9	4.3	4.6	5.1	5.7	5.1	5.1
K ₂ SO ₄	6.0	6.0	6.0	6.0	6.0	1.0	3.0
Glycerol	5.0						
Borax	3.5						
Dequest 2066® (as 100%)	0.4						
Silicon DB100	0.1						
Savinase®	0.3						
Amylase	0.1						
Tinopal® CBS-X	0.1						
Perfume	0.3						
Deflocculating polymer (if any)	0/1.0						
Water	up to 100						
pH	8.3-8.8						

Table 1r

Composition of basic formulations							
Ingredient	Basic formulation (%w/w)						
	78	79	80	81	82	83	84
Na Dobs	14.4	10.3	6.2	9.2	11.3	10.3	10.3
Synperonic A7	11.6	19.3	27.0	17.3	21.3	19.3	19.3
Na Oleate	8.7	6.2	3.7	5.6	6.9	6.2	6.2
Na Laurate	5.9	4.3	2.6	3.8	4.7	4.3	4.3
Na-citrate.2aq	10.0	10.0	10.0	10.0	10.0	6.0	12.0
Glycerol	5.0						
Borax	3.5						
Dequest 2066 (as 100%)	0.4						
Silicon DB100	0.1						
Savinase	0.3						
Amylase	0.1						
Tinopal CBS-X	0.1						
Perfume	0.3						
Deflocculating polymer (if any)	0/1.0						
Water	up to 100						
pH	7.0-9.8						

Table 1s

Composition of basic formulations							
Ingredient	Basic formulation (%w/w)						
	85	86	87	88	89	90	91
Na Dobs	14.4	10.3	11.3	9.2	11.3	10.3	10.3
Synperonic A7	11.6	19.3	17.4	17.3	21.3	19.3	19.3
Na Oleate	8.7	6.2	6.9	5.6	6.9	6.2	6.2
Na Laurate	5.9	4.3	4.7	3.8	4.7	4.3	4.3
Na-CMOS (75%)	10.0	10.0	10.0	10.0	10.0	8.0	12.0
Glycerol	5.0						
Borax	3.5						
Dequest 2066 (as 100%)	0.4						
Silicon DB100	0.1						
Savinase	0.3						
Amylase	0.1						
Tinopal CBS-X	0.1						
Perfume	0.3						
Deflocculating polymer (if any)	0/1.0						
Water	up to 100						
pH	8.2 - 9.0						

Table 1t

Composition of basic formulations		
Ingredient	Basic formulation (%w/w)	
	92	93
NaDobs	10.2	-
K Dobs	-	10.7
Synperonic A7	19.3	19.3
Na Oleate	10.3	-
K Oleate	-	10.9
Glycerol	5.0	5.0
Borax	3.5	3.5
Na-citrate 2aq	10.0	-
Na ₂ CO ₃	-	4.0
Sokalan® CP5	2.5	-
Dequest 2066 (as 100%)	0.4	0.4
Silicon DB100	0.3	0.3
Tinopal® CBS-X	0.5	0.5
Savinase®	0.3	0.3
Amylase	0.1	0.1
Perfume	0.1	0.1
Dye	0.3	0.3
Deflocculating polymer (in any)	0/1.0	0/1.0
water	up to 100	

B. PREPARATION OF POLYMERS

The following is the method used to prepare the polymer hereinafter designated by the reference A-15. All other polymers of Table 2a-2g can be prepared in principle in an analogous manner.

A monomer mixture was prepared consisting of a hydrophilic monomer (acrylic acid 216g, 3.0 moles) and a hydrophobic monomer (Methacrylester 13 (Trade Mark), average chain length 13 carbon atoms, available from Rohm, 32g, 0.12 moles). This gave a molar ratio of hydrophilic to hydrophobic monomer of 25:1.

To a 2 litre glass round bottomed reaction vessel, equipped with a condenser, stainless steel paddle stirrer, and thermometer, was added 600 g of an aqueous mixture of isopropanol and water, consisting of 400 g deionized water and 200g isopropanol. This gave a molar ratio of water, cosolvent mixture to total weight of monomers of 2.42:1 and a water to isopropanol ratio of 2:1.

The monomer mixture was pumped into the reaction vessel over a period of about 3 hours, keeping the reaction mass at 80-85°C, with simultaneous introduction over a period of 4 hours, by pumping in an independent stream, of an initiator solution consisting of 100g of a 4% aqueous solution of sodium persulphate.

After addition of the initiator, the ratio of water and cosolvent to polymer had risen to 2.81:1 and the water to isopropanol ratio to 2.5:1. The reaction contents were held at 80-85°C for a period of about one further hour, giving a total time from the start of the monomer and initiator additions of about 5 hours.

The isopropanol was then substantially removed from the reaction product by azeotropic distillation under vacuum, until the residual isopropanol content was less than 1% as measured by direct gas solid chromatography using a flame ionization detector.

The polymer was neutralized to approximately pH 7 by adding, at 40°C and below, 230 grams (2.76 moles) of 48% caustic soda solution with water added back as necessary to bring the solids to approximately 35%.

The product was an opaque viscous product, having a solids content of approximately 35% and a viscosity of 1500 cps at 23°C as measured by a Brookfield Synchro-Lectric viscometer model RVT, spindle 4, at 20 rpm.

The molecular weight distribution of the polymer produced was measured by aqueous gel permeation chromatography, using an ultra violet detector set at 215 nm. The number average (Mn) and weight average (Mw) molecular weights were measured from the chromatogram so produced, using fractionated sodium polyacrylate standards to construct a calibration graph. The molecular weight of 25 these standards had been measured by the absolute intrinsic viscosity method described in the aforementioned reference of Noda, Tsuge and Nagasawa.

The polymer produced had a Mn of 1600 and Mw of 4300. The pH of the product was 7.0 and an 0.25 % by weight solution on solids had a turbidity of 110 N.T.U.'s.

In the following Tables 2a, 2b, 2c, the structures of various deflocculating polymers are given using the notation of the general formula (I). Co-polymers are designated by the prefix A- (Tables 2a, 2b) whilst multi-polymers are designated by the prefix B- (Table 2c).

In Table 2b, although the polymers are stated to be sodium salts ($A^1, A^4 = Na$), some samples are only partially neutralised (some of $A^1, A^4 = H$). The degree of neutralisation is indicated by way of the approximate pH of the sample.

Instead of quoting a value for n according to formula (I-VII), we prefer to specify the weight average molecular weight (MW) as measured by GPC with polyacrylate standards as hereinbefore described. It is believed that this will be more meaningful to those skilled in the art.

In each Table, some moieties are common to each sample thus:-

Table 2a: y is zero, R^1 is $-CO-O-$ and A^1 is Na.

Table 2b: y is zero, R^1 is $-Co-o-$, R^2 and R^3 are absent and A^1 is Na.

Table 2c: y is zero, R^3 is absent, R^5 is $-H$ and A^1 is Na.

Table 2d: R^1 is $-CO-O-$, R^2 and R^3 are absent, R^4 is $-C_{12}H_{25}$, R^6 is methyl and A^1, A^2 and A^3 are all Na.

Table 2a

Basic Structures of Deflocculating Polymers: general formula I

Polymer Type	\bar{X}	R^2	R^3	R^4	R^5	R^6	MW
A-1	62	$-(C_2H_4O)_5^-$	-Ph-	$-C_9H_{11}$	-H	-H	2.3
A-2	82	$-(C_2H_4O)_{10}^-$	-Ph-	"	-H	-H	1.5
A-3	6	$-(C_2H_4O)_3^-$	-	$-C_{12}H_{25}$	-H	$-CH_3$	1.5
A-4	33	$-(C_2H_4O)_{11}^-$	-	$-C_{17}H_{35}$	-H	$-CH_3$	1.5
A-5	8	$-(CH(C_2H_5)CH_2O)_6^-$	-	-H	-H	$-CH_3$	1.5
A-6	25	"	-	-H	-H	$-CH_3$	1.5
A-7	100	$-(C_2H_4O)_7^-$	-	$-C_{12}H_{25}$	-H	$-CH_3$	3.6
A-8	50	"	-	"	-H	$-CH_3$	2.7
A-9	25	"	-	"	-H	$-CH_3$	1.8
A-10	12	"	-	"	-H	$-CH_3$	1.2
A-11	25	-	-	"	-H	$-CH_3$	1.5
A-12	25	$-(CH(CH_3)CH_2O)_6^-$	-	-H	-H	$-CH_3$	2.7
A-13	25	-	-	$-CH(C_2H_5)C_5H_{11}$	-H	-H	1.5
A-14	17	$-(C_2H_4O)_3^-$	-	$-C_{12}H_{25}$	$-CO_2Na$	$-CH_3$	1.5
A-15	25	-	-	"	-H	$-CH_3$	1.5
A-16	25	$-(CH(C_2H_5)CH_2O)_6^-$	-	-H	-H	$-CH_3$	1.5

Table 2b

Basic Structures of Deflocculating Polymers: general formula I

Polymer Type	X	Approx. pH	R ⁴	R ⁵	R ⁶	MW (cf n)
A-17	50	7	-C ₁₂ H ₂₅	-H	-CH ₃	3.6K
A-18	100	7	"	-H	-CH ₃	3.0K
A-19	25	5	"	-H	-CH ₃	15.2K
A-20	50	5	"	-H	-CH ₃	15.0K
A-21	100	5	"	-H	-CH ₃	14.2K
A-22	25	4.9	"	-H	-CH ₃	8.7K
A-23	25	3.8	"	-H	-CH ₃	32.0K
A-24	25	7	"	-H	-CH ₃	5.0K
A-25	25	7	-C ₁₀ H ₂₁	-H	-CH ₃	4.2K
A-26	25	4.3	-C _{16/18} H _{33/37}	-H	-CH ₃	21.0K
A-27	25	4.3	-C ₁₀ H ₂₁	-H	-CH ₃	20.4K
A-28	25	7	-C _{16/18} H _{33/37}	-CO ₂ Na	-H	5.9K
A-29	8.8	7	-C ₈ H ₁₇	"	-H	4.1K
A-30	25	7	-C ₁₂ H ₂₅	"	-H	3.0K
A-31	8.8	7	"	"	-H	3.1K
A-32	25	7	-C ₁₈ H ₃₇	"	-H	5.2K
A-33	8.8	7	"	"	-H	6.2K

Table 2b (continued)
Basic structures of Deflocculating Polymers

Polymer Type	X	R ⁴	R ⁵	R ⁶	MW (cf n)
A-34	500	-C ₁₂ H ₂₅	-H	-CH ₃	4.5K
A-35	250	"	"	"	5.5K
A-36	12	"	"	"	4.1K
A-37	6	"	"	"	3.2K
A-38	500	"	"	"	27K
A-39	250	"	"	"	21K
A-40	12	"	"	"	20K
A-41	6	"	"	"	27K
A-42	500	"	"	"	53K
A-43	250	"	"	"	58K
A-44	50	"	"	"	7.5K
A-45	25	"	"	"	7.2K

Table 2c

Basic structures of deflocculating polymers: general formula I

Polymer Type	\bar{M}	Approx. pH	R ¹	R ²	R ³	R ⁴	R ⁵ Mw (G/m)
A-46	25	6.8	-O-CO-	-	-	-C ₁₂ H ₂₅	4.4
A-47	25	7.2	-O-CO-	-	-	-(C(CH ₃)(C ₂ H ₅)(C ₆ H ₁₁))-	4.6
A-48	25	7.2	-O-	-(C ₂ H ₅ O) ₄ (CH(CH ₃)(CH ₂ O) ₁₂ -H)	-	-	4.5
A-49	25	4.5	-O-	-(C ₂ H ₅ O) ₄ (CH(CH ₃)(CH ₂ O) ₂₄ -H)	-	-	3.1

Table 2d

Basic Structures of Deflocculating Polymers: General

Polymer Type	X	Y	R ⁵	M _n
B-1	46	13	-H	5.3
B-2	46	13	-H	5.3
B-3	46	13	-H	5.3
B-4	32	21	-H	5.3
B-5	21	5.9	-H	5.3
B-6	21	5.9	-H	5.3
B-7	8	5.3	-H	6.2
B-8	8	5.3	-H	3.1
B-9	16.8	11.2	-COO ¹	2.8

Table 2e: R¹ is -CO-O-, R² and R³ are absent,
R⁴ is -Cl₂H₂₅, R⁵ is -H, R⁶ is -CH₃,
q is zero and A¹-A³ are Na.

Table 2f: y is zero, R² and R³ are absent, R⁴ is
-Cl₂H₂₅, R⁵ is -H, R⁶ is -CH₃, R⁷ and
are -H, A¹ is Na.

Table 2g: y is zero, R¹ is -CO-O-, R² and R³ are
absent, R⁴ is -Cl₂H₂₅, R⁵ is -H, R⁶ is
CH₃ and A¹-A³ are Na.

Table 2h: R² and R³ are absent, A¹ is Na.

Table 2k: R² and R³ are absent; R⁵ and R⁶ are -H;
A¹ is -H or a branching point; and in the
molecular entities of formula (III) in
the side-chain R¹, 5-6 are as above and R⁴
is -H.

Table 2e

Basic Structures of Deflocculating Polymers: general formula (1)

Polymer Type	X	Y	P	q	R ¹	R ²	R ³	R ⁴	R ⁵
B-10	25	0	1	0	-CH ₃	-	-	-	-CO-O-(C ₂ H ₄ O) ₁₇ -H
B-11	0	0	25	0	-H	-	-	-	-CO-O-C ₂ H ₄ OH
B-12	13.9	9.2	1	0	-H	-	-	-	-SO ₃ Na
B-13	22.5	0	2.5	0	-H	-	-	-	-SO ₃ Na
B-14	22.5	0	2.5	0	-CH ₃	-	-	-	-CO-O-C ₂ H ₄ -OSO ₃ Na
B-15	22.5	0	2.5	0	-H	-	-	-	-CO-NH-C(C ₂ H ₅) ₂ -SO ₃ Na

Table 2f
Basic Structures of Deflocculating Polymer: general formula II

Polymer Type	x	p	q	R ¹	R ⁹	R ¹⁰	MW (cf. n)	Reference
							estimated	
B-16	0	25-500	0	-CO-O-	-CO-NH ₂ -	-	40K	US A 4,528,348
B-17	0	25-500	0	-CO-NH-	-CO-NH ₂ -	-	40K	US A 4,520,182
B-18	25-500	25-500	0	-CO-O-	-CO-NH ₂ -	-	40K	US A 4,521,580
B-19	25-500	25-500	0	-CO-NH-	-CO-NH ₂ -	-	40K	
B-20	25-500	25-500	0	-CO-O-	-OH	-	3-60K	
B-21	25-500	25-500	25-500	-CO-O-	-OH	-O-CO-CH ₃	3-60K	

Table 2g

Basic Structures of Deflocculating Polymers: general formula II
with introduction of some branching by TMPTA

Polymer Type	X	r	$\frac{Q^1}{Q^2}$	TMPTA	$\frac{M_w}{M_n}$
B-22	25	0.25		TMPTA	3.25
B-23	25	0.50		TMPTA	3.15
B-24	25	0.75		TMPTA	3.15

Table 2h

Basic Structures of Deflocculating Polymers: general formula IV

Polymer Type	x + y	R ¹	R ⁴ estimated	R ¹¹	R ¹²	MW (cf. n). Reference
B-25	6-20	-NH-CO- or CH ₂ -O-CO-	-C ¹ ₂ H ₂₅	-NH-CO-CH ₃ , -COO ¹ or -OH	-CH ₂ OH or -COO ¹	30K Biosan LP31 (ex Petroferm)

Table 2k
Basic Structures of Deflocculating polymers: general formula III

Polymer type	x	z	R ¹	R ⁴	MW (cf. n)
A-50	25	1	-O-	-C ₁₂ H ₂₅	2.1 k

Effect of deflocculating polymers on physical properties
of liquid detergent formulations.

<u>Example</u>	<u>Basic</u> <u>Compo-</u> <u>sition</u>	<u>Polymer</u> <u>Type</u>	<u>η</u>	<u>Product</u> <u>Stability</u>	<u>Viscosity</u> <u>m Pas at</u> <u>21s-1</u>
1	1	-	-	Unstable	1430-1740
2	1	A-1	0.5	Stable	260
3	1	A-1	1.0	Stable	100
4	1	A-1	2.0	Stable	140
5	1	A-2	0.5	Stable	260
6	1	A-2	1.0	Stable	70
7	1	A-2	2.0	Stable	100
8	1	A-3	0.5	Stable	280
9	1	A-3	1.0	Stable	440
10	2	-	-	Unstable	2560
11	2	A-1	0.5	Stable	35
12	2	A-1	1.0	Stable	35
13	2	A-1	2.0	Stable	35
14	2	A-2	0.5	Stable	35
15	2	A-2	1.0	Stable	35
16	2	A-2	2.0	Stable	35
17	2	A-4	0.5	Stable	80
18	2	A-4	1.0	Stable	110
19	2	A-4	2.0	Stable	210
20	1	-	-	Unstable	1430-1740
21	1	A-14	0.25	Stable	130
22	1	A-14	0.50	Stable	70
23	1	A-14	1.0	Stable	35
24	1	A-14	2.0	Stable	60

Example	Basic Compo- sition	Polymer Type	Con- c.	Product Stability	Viscosity in Pas at 25°C
10	25	1	A-5	0.5	Stable 480
	26	1	A-4	0.5	Stable 340
	27	1	A-4	1.0	Stable 440
	28	1	A-4	2.0	Stable 130
15	29	3	-	-	Unstable 500
	30	3	A-1	0.5	Stable 290
	31	3	A-1	1.0	Stable 1220
20	32	3	A-1	2.0	Stable 1520
	33	3	A-2	0.5	Stable 530
	34	4	-	-	Unstable 1600
	35	4	A-1	0.5	Stable 630
25	36	4	A-2	0.5	Stable 500
	37	8	-	-	Unstable 190
	39	8	A-2	1	Stable 1570
30	40	9	-	-	Unstable 90
	41	9	A-2	1	Stable 610
	42	10	-	-	Unstable 40
35	43	10	A-2	1	Stable 240
	44	5	-	-	Unstable 1380
	45	5	A-2	1	Stable 200
	46	6	-	-	Unstable 2400
40	47	6	A-2	1	Stable 70
	48	7	-	-	Unstable 2300
	49	7	A-2	1	Stable 40
45	50	2	-	-	Unstable 2560
	51	2	A-2	1	Stable 60
	52	6	-	-	Unstable 1600-2070
50	53	6	A-7	0.50	Stable 80
	54	6	A-7	1.0	Stable 100
	55	6	A-7	2.0	Stable 120
55					

Example	Basic Compo- sition	Polymer Type	Product Stability	Viscosity in Pas at 21s-1
56	6	A-8	0.25 Stable	160
57	6	A-8	0.50 Stable	190
58	6	A-8	1.0 Stable	460
59	6	A-11	0.5 Stable	700
60	6	A-11	1.0 Stable	760
61	2	-	- Unstable	1160-2560*
62	2	A-7	0.5 Stable	130
63	2	A-7	1.0 Stable	80
64	2	A-7	2.0 Stable	120
65	2	A-8	1.0 Stable	100
66	2	A-8	2.0 Stable	120
67	2	A-9	0.5 Stable	150
68	2	A-9	1.0 Stable	110
69	2	A-9	2.0 Stable	200

Example	Basic Concn g/100g	Polymer Type	η	Product Stability	Viscosity mPas at 25°C
70	2	-	-	Unstable	1160-2560
10 71	2	A-10	0.5	Stable	130
72	2	A-10	1.0	Stable	330
73	2	A-11	1.0	Stable	140
74	2	A-11	2.0	Stable	210
75	6	-	-	Unstable	1600-2070*
76	6	A-12	2.0	Stable	70
77	6	A-6	1.0	Stable	50
20 78	6	A-6	2.0	Stable	70
79	6	A-13	2.0	Stable	70
25 80	2	-	-	Unstable	1160-2560*
81	2	A-12	2.0	Stable	80
82	2	A-6	1.0	Stable	100
30 83	2	A-6	2.0	Stable	100
84	2	A-13	2.0	Stable	90
35 85	11	-	-	Unstable	**
86	11	A-12	1.0	Stable	120
87	11	A-12	2.0	Stable	120
40 88	11	A-13	2.0	Stable	120
45 89	12	-	-	Unstable	**
90	12	A-1	0.1	Stable	20
91	12	A-1	2.0	Stable	70
50					

		Polymer		Product	Viscosity
		Type		Stability	m Pa.s at
					21s-1
	92	13	-	Unstable	660
	93	13	A-2	0.5 Stable	540
	94	13	A-2	1.0 Stable	600
	95	14	-	Unstable	700
15	96	14	A-2	1.0 Stable	160
	97	14	A-2	2.0 Stable	700
	98	15	-	Unstable	2240
	99	15	A-2	2.0 Stable	300
20	100	16	-	Unstable	>9000
	101	16	A-2	2.0 Stable	150
	102	17	-	Unstable	730
25	103	17	A-2	0.5 Stable	300
	104	17	A-2	1.0 Stable	990
	105	18	-	Unstable	2490
30	106	18	A-2	0.5 Stable	100
	107	18	A-2	1.0 Stable	510
	108	18	A-2	2.0 Stable	380
	109	19	-	Unstable	950
35	110	19	A-2	0.5 Stable	670
	111	20	-	Unstable	950
	112	20	A-2	2.0 Stable	1430
40	113	21	-	Unstable	2730
	114	21	A-1	0.5 Stable	750
	115	22	-	Unstable	5550
45	116	22	A-1	0.5 Stable	430
	117	23	-	Unstable	6630
	118	23	A-1	0.5 Stable	220
	119	24	-	Unstable	7950
50	120	24	A-1	0.5 Stable	270
	121	25	-	Unstable	8620
	122	25	A-1	0.5 Stable	270

Example	Basic Compo- sition	Reverber- ation	Reverber- ation	Reverber- ation	Reverber- ation
123	26	-	-	Unstable	5970
124	26	A-1	0.5	Stable	800
125	26	-	-	Unstable	5970
126	26	A-6	1.0	Stable	700
127	26	A-7	0.5	Stable	1080
128	26	A-8	0.5	Stable	1510
129	26	A-11	0.5	Stable	1060
130	27	-	-	Unstable	5050
131	27	A-1	0.25	Stable	760
132	27	A-1	0.50	Stable	660
133	27	A-1	0.75	Stable	850
134	27	A-1	1.0	Stable	1180
135	27	A-11	0.50	Stable	660
136	27	A-11	0.75	Stable	750
137	27	A-11	1.0	Stable	850
138	29	-	-	Stable	>9000
139	29	A-11	0.5	Stable	1060
140	30	-	-	Stable	>9000
141	30	A-11	0.5	Stable	900
142	31	-	-	Stable	>9000
143	31	A-11	0.5	Stable	1820
144	32	-	-	Stable	>9000
145	32	A-11	0.5	Stable	1240
146	33	-	-	Stable	>9000
147	33	A-11	0.5	Stable	810
148	34	-	-	Unstable	170
149	34	A-2	1	Stable	1400
150	35	-	-	Unstable	6000
151	35	A-2	0.5	Stable	350
152	35	A-2	1	Stable	600
153	35	A-2	2	Stable	2000

Phoneme	Basic Compo- sition	Phoneme Type	Phoneme Stability	Phoneme Stability	Phoneme Stability
---------	---------------------------	-----------------	----------------------	----------------------	----------------------

154	36	A-11	0.75	Stable	1820
155	37	A-11	0.75	Stable	1810
156	38	A-11	0.75	Stable	1750
157	39	A-11	0.75	Stable	1590
158	40	A-11	0.75	Stable	1500

159	41	A-11	0.75	Stable	1860
160	42	A-11	0.74	Stable	1670
161	43	A-11	0.72	Stable	1530
162	44	A-11	0.69	Stable	1400
163	45	A-11	0.65	Stable	1490***

164	6	A-16	1	Stable	50
165	6	A-16	2	Stable	70
166	2	A-16	1	Stable	100
167	2	A-16	2	Stable	100

168	2	A-46	1	Stable	60
169	2	A-47	1	Stable	50
170	2	A-47	2	Stable	50
171	2	A-48	2	Stable	1160
172	2	A-49	2	Stable	2440

173	2	A-34	2	Stable	60
174	2	A-35	2	Stable	70
175	2	A-18	0.5	Stable	75
176	2	A-18	1.0	Stable	40
177	2	A-18	2.0	Stable	40
178	2	A-11	0.5	Stable	70
179	2	A-11	1.0	Stable	70
180	2	A-11	2.0	Stable	60
181	2	A-36	1.0	Stable	90
182	2	A-36	2.0	Stable	80

Sample	Days in Clemson Station	Specimen No.	Age	Stability	Accuracy in lbs. and oz.
183	2	A-37	2.0	Stable	1980
184	2	A-38	1.0	Stable	125
185	2	A-39	2.0	Stable	310
186	2	A-21	0.5	Stable	100
187	2	A-21	1.0	Stable	150
188	2	A-21	2.0	Stable	1280
189	2	A-20	0.5	Stable	75
190	2	A-20	1.0	Stable	220
191	2	A-20	2.0	Stable	6580
192	2	A-19	0.5	Stable	940
193	2	A-19	1.0	Stable	530
194	2	A-19	2.0	Stable	4290
195	2	A-23	0.5	Stable	1090
196	2	A-23	1.0	Stable	1170
197	2	A-23	2.0	Stable	4920
198	2	A-40	0.5	Stable	190
199	2	A-40	1.0	Stable	430
200	2	A-40	2.0	Stable	4700
201	2	A-41	1.0	Stable	300
202	2	A-41	2.0	Stable	1580
203	2	A-42	1.0	Stable	120
204	2	A-42	2.0	Stable	350
205	2	A-43	2.0	Stable	4150
206	46-48	-	-	Unstable	4000-6000*
207	46	A-11	0.5	Stable	90
208	46	A-11	1.0	Stable	110
209	47	A-11	1.0	Stable	620
210	48	A-11	1.0	Stable	2230
211	38	-	-	Unstable	5000-6000*
212	38	A-11	1.0	Stable	560
213	38	A-18	0.5	Stable	460
214	38	A-18	1.0	Stable	510
215	38	A-19	0.3	Stable	1240
216	38	A-19	0.5	Stable	1040

	<u>Example</u>	<u>Basic Compo- sition</u>	<u>Polymer Type</u>	<u>Product Stability</u>	<u>Viscosity mPas at 21s⁻¹</u>
5					
	217	38	A-19	1.0 Stable	3230
	218	38	A-21	0.5 Stable	670
10	219	38	A-21	1.0 Stable	1260
	220	50	A-11	0.75 Stable	730
	221	49	A-11	0.5 Stable	1510
15	222	49	A-11	0.75 Stable	770
	223	49	A-11	1.0 Stable	730
	224	49	A-45	0.75 Stable	820
	225	49	A-21	0.75 Stable	1060
20	226	49	A-21	0.40 Stable	2510
	227	49	A-17	0.75 Stable	880
	228	49	A-17	1.50 Stable	1510
25	229	49	A-36	0.75 Stable	680
	230	49	A-44	0.75 Stable	880
	231	49	A-24	0.75 Stable	540
	232	49-55	-	- Unstable	4000-6000*
30	233	51	A-11	0.75 Stable	800
	234	52	A-11	0.75 Stable	650
	235	53	A-11	0.75 Stable	680
35	236	54	A-11	0.75 Stable	790
	237	55	A-11	0.65 Stable	600
	238	56-57	-	- Unstable	Not measured
	239	56	A-11	0.25 Stable	880
40	240	57	A-11	0.25 Stable	550
	241	58	-	- Unstable	140
	242	58	A-11	0.5 Stable	1300
45	243	58	A-11	2.0 Stable	2240
	244	58	A-36	0.5 Stable	230
	245	58	A-36	2.0 Stable	140
	246	59	-	- Unstable	80
50	247	59	A-11	0.5 Stable	270
	248	59	A-11	2.0 Stable	1190
	249	59	A-36	0.5 Stable	70
55	250	59	A-36	2.0 Stable	120

EP 0 346,995 B1

	Example	Basic Compo- sition	Polymer Type	ξ	Product Stability	Viscosity mPas at $21s^{-1}$
5	251	60	-	-	Stable	520
10	252	60	A-36	0.5	Stable	380
	253	60	A-36	2.0	Stable	220
	254	60	A-36	4.0	Stable	210
	255	61	-	-	Unstable	340
15	256	61	0.5	A-11	Stable	780
	257	61	0.5	A-17	Stable	1370
	258	61	0.5	A-18	Stable	400
20	259	62	-	-	Unstable	4000-6000*
	260	62	0.5	A-11	Stable	940
	261	63	0.5	A-11	Stable	740
	262	2	2.0	B-1	Stable	100
25	263	2	4.0	B-1	Stable	360
	264	2	2.0	B-10	Stable	1490
	265	5	2.0	B-11	Stable	50
	266	2	2.0	B-22	Stable	200
30	267	2	2.0	B-23	Stable	140
	268	2	2.0	B-24	Stable	200
	269	5	2.0	B-25	Stable	1790
35	270	64-91	-	-	Unstable	4000-6000*
	271	64	1.0	A-11	Stable	190
	272	65	1.0	A-11	Stable	2290
	273	66	1.0	A-11	Stable	850
40	274	67	1.0	A-11	Stable	230
	275	68	1.0	A-11	Stable	440
	276	69	1.0	A-11	Stable	1130
45	277	70	1.0	A-11	Stable	230
	278	71	1.0	A-11	Stable	190
	279	72	1.0	A-11	Stable	570
	280	73	1.0	A-11	Stable	370
50	281	74	1.0	A-11	Stable	290
	282	75	1.0	A-11	Stable	600
	283	76	1.0	A-11	Stable	140
55	284	77	1.0	A-11	Stable	700

285	78	1.0	A-11	Stable	290
286	79	1.0	A-11	Stable	260
287	80	1.0	A-11	Stable	320
288	81	1.0	A-11	Stable	250
289	82	1.0	A-11	Stable	470
290	83	1.0	A-11	Stable	480
291	84	1.0	A-11	Stable	300
292	85	1.0	A-11	Stable	160
293	86	1.0	A-11	Stable	250
294	87	1.0	A-11	Stable	240
295	88	1.0	A-11	Stable	340
296	89	1.0	A-11	Stable	360
297	90	1.0	A-11	Stable	610
298	91	1.0	A-11	Stable	190
299	92/93	-	-	Unstable	4000-6000*
300	92	1.0	A-11	Stable	1000
301	93	1.0	A-11	Stable	220
302	5	2.0	A-50	Stable	350

* Unreliable results due to rapid phase separation.

** Cannot be measured due to very rapid phase separation.

*** After 11 days storage; product shows increase of viscosity due to stirring/shear.

Although not specified, similar results can be obtained with Deflocculating Polymers with structures A25-33, B2-9 and B12-21

Electron Micrographs

The appended micrographs show the effect of deflocculating polymers on the lamellar droplets. Photographs 1, 4 and 7 show flocculated droplets without the polymer. Photographs 2, 3, 5, 6 and 8 show the deflocculating effect of the polymer in compositions according to the present invention.

DESCRIPTION OF PHOTOGRAPHS

- Photograph 1 - EM-micrograph of part of a floc of lamellar droplets, i.e. the droplets are strongly flocculated. Part of the continuous electrolyte phase is visible.
Basic formulation 1, without "deflocculating" polymer;
- Photograph 2 - EM-micrograph of basic formulation 1, with 1% of "deflocculating" polymer A-2. The individual character of the droplets, i.e. the "deflocculating" effect of the polymer, is beautifully demonstrated. Compare with Photo 1;
- Photograph 3 - As photograph 2, but with 0,5% "deflocculating" polymer A-5;
- Photograph 4 - EM-micrograph of part of a floc of lamellar droplets, i.e. the droplets are strongly flocculated. The continuous electrolyte phase is not visible. Basic formulation 2, without "deflocculating" polymer;
- Photograph 5 - EM-micrograph of basic formulation 2, with 2% of "deflocculating" polymer A-7. The individual character of the droplets, i.e. the "deflocculating" effect of the polymer, is beautifully demonstrated. Compare with Photograph 4;
- Photograph 6 - As photograph 5, but with "deflocculating" polymer A-11;
- Photograph 7 - EM-micrograph of basic formulation 49 without "deflocculating" polymer. The flocculation of the lamellar droplets can be detected in two ways: - flocculation as such as; - the continuous electrolyte phase (A) is irregularly divided over the sample.
- Photograph 8 - EM-micrograph of basic formulation 49 with 0.75% of "deflocculating" polymer A-11. The individual character of the lamellar droplets, i.e. the "deflocculating" effect of the polymer, is beautifully demonstrated. Compare with Photograph 7.

Table 3

Raw Material Specification	
Component	Specification
NaDoBS	Na Dodecyl Benzene Sulphonate
LES	Lauryl ether sulphate
Synperonic A7	C ₁₂₋₁₅ ethoxylated alcohol, 7EO, ex ICI
Synperonic A3	C ₁₂₋₁₅ ethoxylated alcohol, 3EO ex ICI
STP	Sodium Tripolyphosphate
KTP	Potassium Tripolyphosphate
Silicone oil	Foam depressor, ex Dow Corning
Gasil 200	Corrosion inhibitor, ex Crossfield
Na-SCMC	Na Carboxymethyl cellulose (Anti-redeposition agent)
Tinopal CBS-X	Fluorescer, ex Ciba-Geigy
Blankophor RKH 766	Fluorescer, ex Bayer
Dequest 2060S/2066	Metal chelating agent, ex Monsanto
Alcalase 2.5L	Proteolytic enzyme, ex Novo

Component	Specification
Dobanol 23-6.5	C ₁₂₋₁₃ ethoxylated alcohol, 6.5 EO, ex shell
Neodol 23-6.5	as Dobanol 23-6.5
TriEA	Triethanolamine
Zeolite A ₄	Wessalith P, ex Degussa
Na-CMOS	Carboxy-Methyl-Oxy-Succinate, tri sodium salt

Specification

Acrylic/Maleic builder polymer, ex BASF

Claims

1. A liquid detergent composition which yields no more than 2% by volume phase separation when stored at 25°C for 21 days from the time of preparation and comprises a dispersion of lamellar droplets in an aqueous continuous phase, and also comprising a deflocculating polymer having a hydrophilic backbone and at least one hydrophobic side-chain, with the proviso that

when the composition comprises from 3% to 12% of a potassium alkyl benzene sulphonate, from 2% to 8% of a potassium fatty acid soap, from 0.5 to 5% of a nonionic surfactant, from 1 to 25% of alkalimetal triphosphophate, wherein the alkalimetal is sodium or potassium, and at least 50% by weight of the alkalimetal triphosphophate is sodium triphosphophate, optionally 20-65% of the sodium triphosphophate being replaced by tetrapotassium pyrophosphate, and from 0.1 to 2% of a partially esterified, neutralised co-polymer of maleic anhydride with vinylmethyl ether, ethylene or styrene, all percentages being by weight, the weight ratio of said sulphonate to said soap being from 1:2 to 6:1, the weight ratio of said sulphonate to said nonionic surfactant being from 3:5 to 25:1, the total amount of said sulphonate, soap and nonionic surfactant being from 7.5 to 20% by weight,

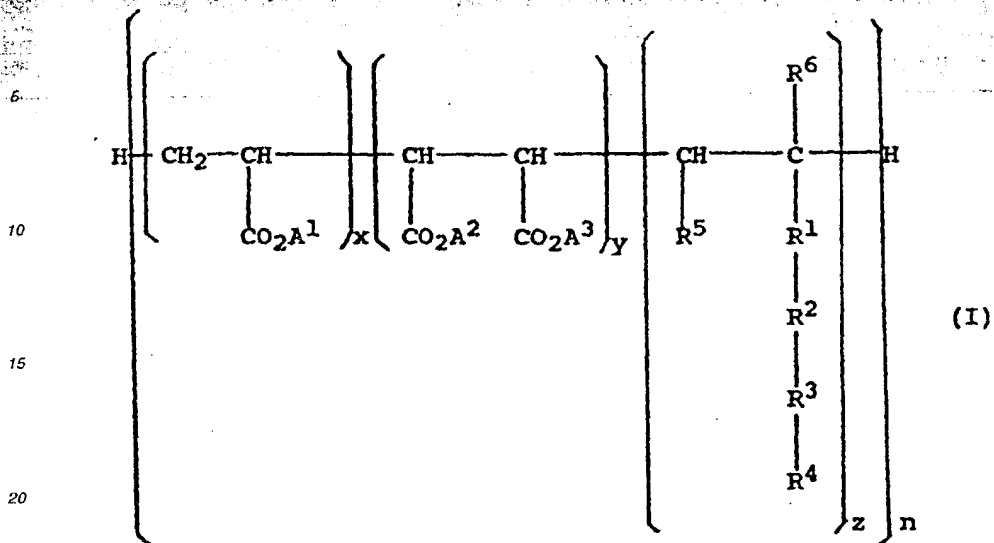
then the decoupling polymer does not consist solely of from 0.1 to 2% by weight of a partially esterified, neutralised co-polymer of maleic anhydride with vinylmethyl ether, ethylene or styrene,

and with the further proviso that

when the composition comprises soap, tetrapotassium pyrophosphate and zwitterionic surfactant,

then the decoupling polymer does not consist solely of an interpolymers of methyl ether vinyl and maleic anhydride esterified with the zwitterionic surfactant.

2. A composition according to claim 1, wherein the polymer has the general formula (I)



25 wherein:

z is 1; $(x + y) : z$ is from 4 : 1 to 1,000 : 1; in which the monomer units may be in random order; y being from 0 up to a maximum equal to the value of x ; and n is at least 1;

30 R¹ represents -CO-O-, -O-, -O-CO-, -CH₂-, -CO-NH- or is absent;

R² represents from 1 to 50 independently selected alkyleneoxy groups, or is absent, provided that when R³ is absent and R⁴ represents hydrogen or contains no more than 4 carbon atoms, then R² must contain an alkyleneoxy group with at least 3 carbon atoms;

R³ represents a phenylene linkage, or is absent;

R⁴ represents hydrogen or a C₁₋₂₄ alkyl or C₂₋₂₄ alkenyl group, with the provisos that

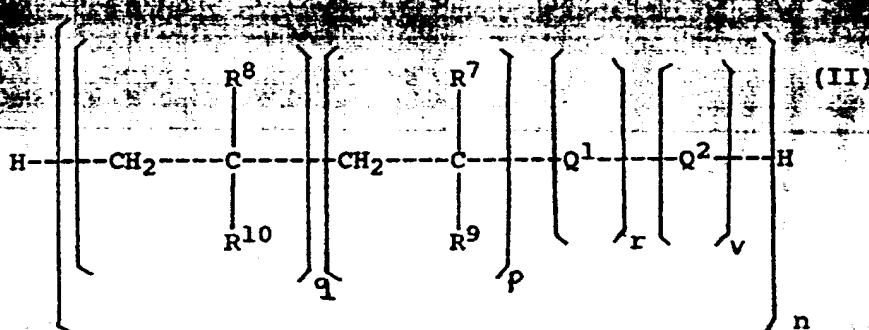
40 a) when a¹ represents -O-CO-, R² and R³ must be absent and R⁴ must contain at least 5 carbon atoms;
b) when R² is absent, R⁴ is not hydrogen and when R³ is absent, then R⁴ must contain at least 5 carbon atoms;

R⁵ represents hydrogen or a group of formula -COOA⁴;

R⁶ represents hydrogen or C₁₋₄ alkyl; and

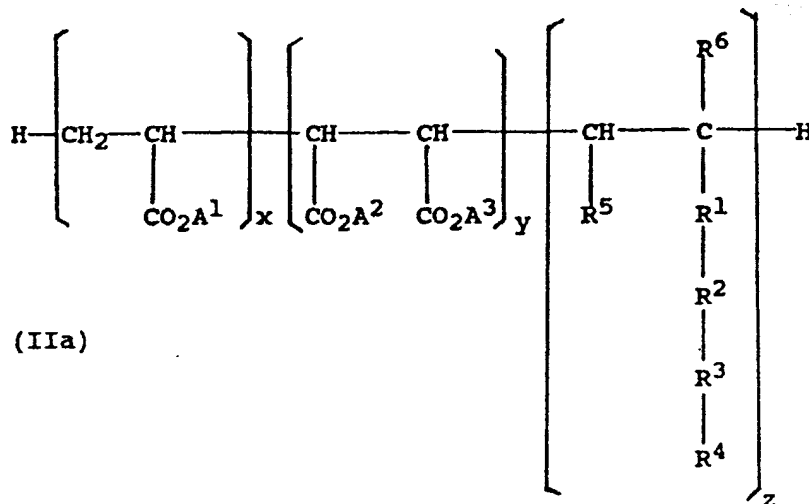
A¹, A², A³ and A⁴ are independently selected from hydrogen, alkali metals, alkaline earth metals, ammonium and amine bases and C₁₋₄ alkyl.

50 or of formula (II):



wherein

Q^2 is a molecular entity of formula (IIa).



wherein z and R^{1-6} are as defined for formula (I); A^{1-4} are as defined for formula (I) or $(\text{C}_2\text{H}_4\text{O})_t\text{H}$, wherein t is from 1-50, and wherein the monomer units may be in random order;

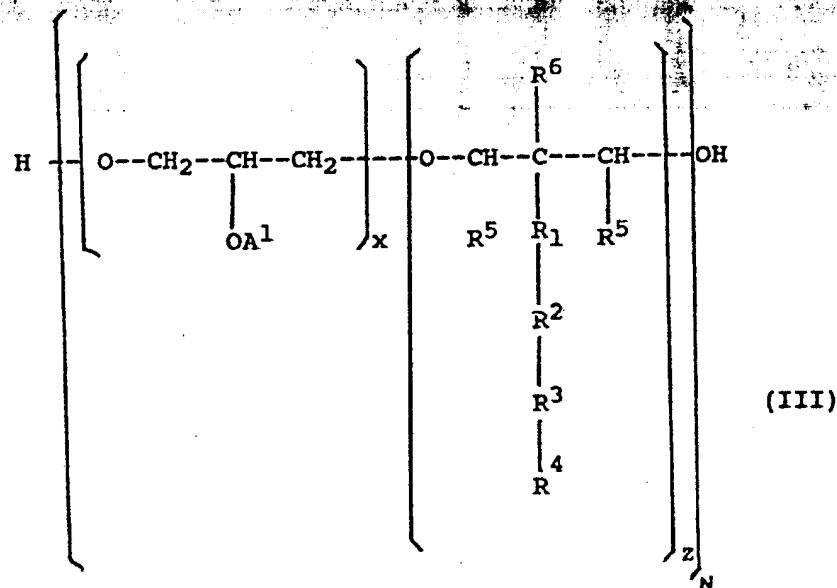
Q^1 is a multifunctional monomer, allowing the branching of the polymer, wherein the monomers of the polymer may be connected to Q^1 in any direction, in any order, therewith possibly resulting in a branched polymer.

n and z are as defined above; $v = 1$ and $(x + y + p + q + r) : z$ is from 4 : 1 to 1,000 : 1, in which the monomer units may be in random order;

R^7 and R^8 represent $-\text{CH}_3$ or $-\text{H}$;

R^9 and R^{10} represent independently groups selected from $-\text{SO}_3\text{Na}$, $-\text{CO}-\text{O}-\text{C}_2\text{H}_4-\text{OSO}_3\text{Na}$, $-\text{CO}-\text{O}-\text{NH}-\text{C}(\text{CH}_3)_2-\text{SO}_3\text{Na}$, $-\text{CO}-\text{NH}_2$, $-\text{O}-\text{CO}-\text{CH}_3$, $-\text{OH}$;

3. A composition according to claim 1 or 2, wherein the polymer is of formula III:

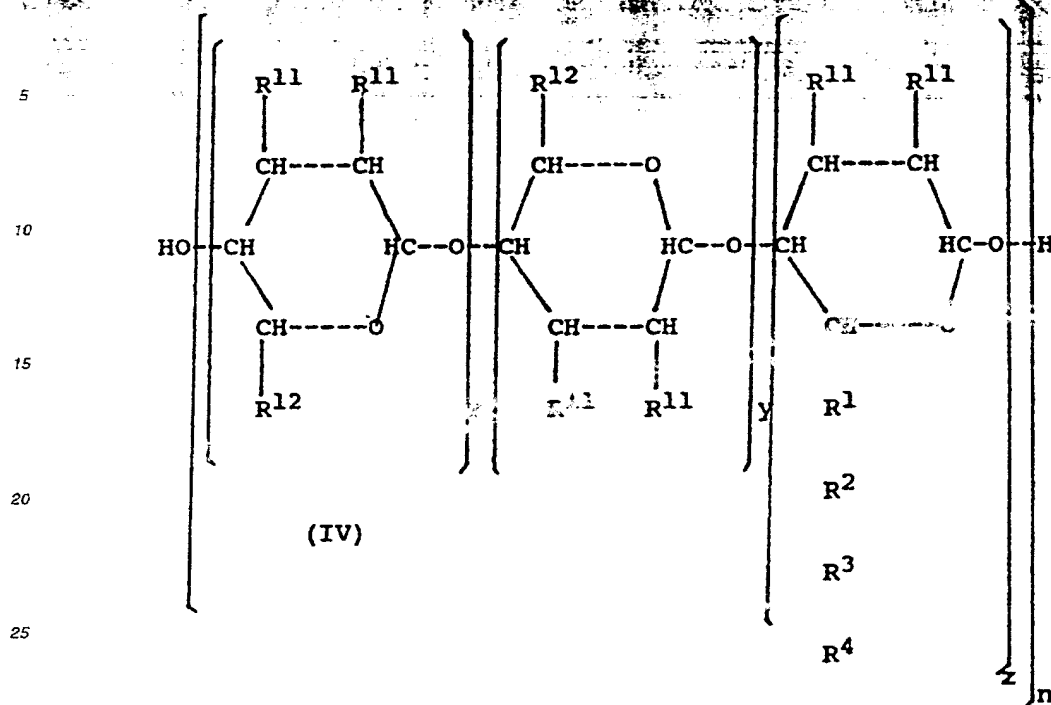


wherein:

x is from 4 to 1,000, n, z and R¹⁻⁶ are as defined in formula I, wherein the monomers units may be in random order;

A¹ is as defined above for formula I, or -CO-CH₂-C(OH)-CO₂A¹-CH₂-CO₂A¹, or may be a branching point where to other molecules of formula (III) are attached.

4. A composition according to claim 1, wherein the polymer is of the formula (IV)



Wherein :

z, n and A¹ are as defined above for formula I; (x+y)z is from 4:1 to 1,000:1, wherein the monomers may be in random order.

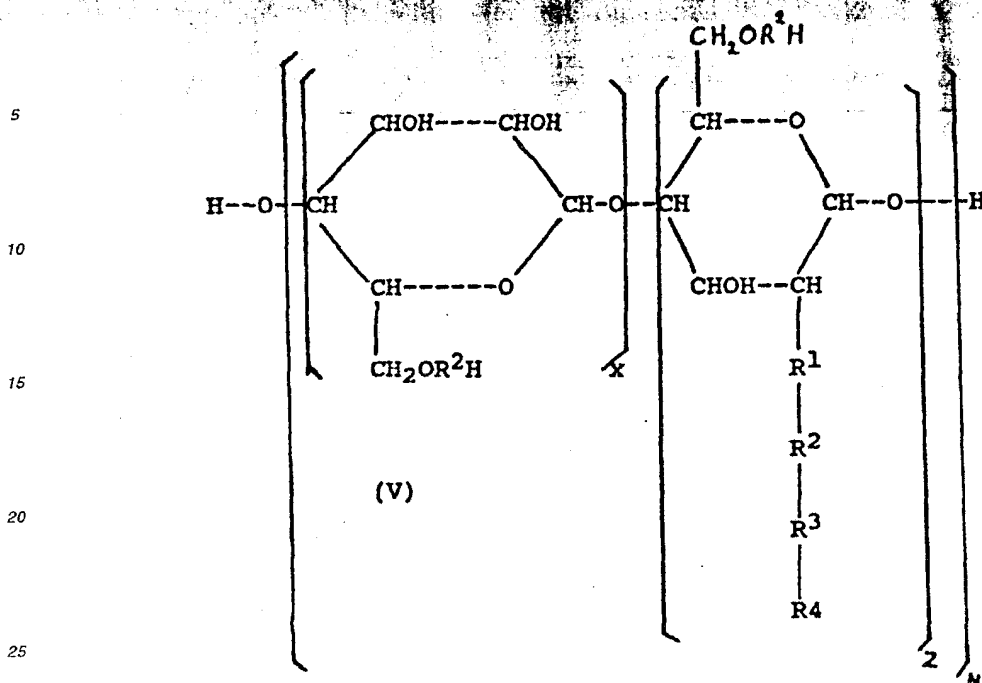
R¹ is as defined above for formula I, or can be -CH₂-O-, -CH₂-O-CO-, -NH-CO-;

R²⁻⁴ are as defined in formula I;

R¹¹ represents -OH, -NH-CO-CH₃, or -OSO₃A¹;

R¹² represents -OH, -CH₂OH, -CH₂OSO₃A¹, COOA¹, -CH₂-OCH₃;

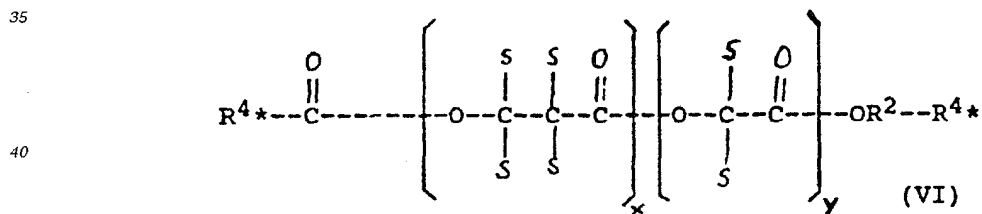
or of formula (V):



Wherein:

z, n and R¹⁻⁶ are as defined above for formula I; and x is as defined for formula III;

5. A composition according to claim 1, wherein the polymer has the formula VI:



wherein:

If z is the total of R⁴ groups, then the ratio (x+y) : z is from 4 : 1 to 1,000 : 1; R⁴ is R⁴ or -H.

R² and R⁴ are as defined above for formula I;

and S is selected from -H, -COOA¹, -CH₂COOA¹, -CH(COOA¹)₂, (CH₂COOA¹)₂H, wherein A¹ is as defined for formula I or is R⁴;

with the proviso that at least one R⁴ group is present as a side chain;

or of formula (VII):



Wherein:

x, z, s and R^4 are as defined above for formula VI:

and wherein at least one R^4 group is present as a side chain; v is 0 or 1

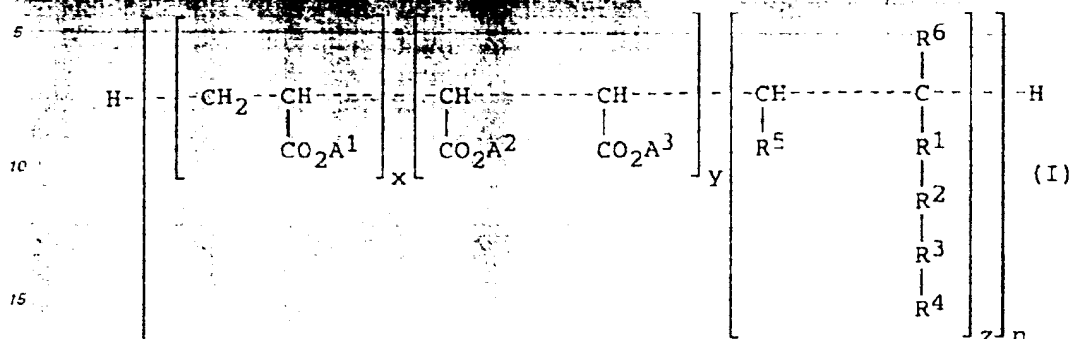
6. A composition according to one or more of the preceding claims, wherein the average molecular weight of the polymer is from 500 to 500,000 as determined by gel permeation chromatography, using polyacrylate standards.
7. A composition according to claim 6, wherein said average molecular weight is from 1000 to 30,000.
8. A composition according to any preceding claim, wherein the total amount of deflocculating polymer is from 0.01 to 5% by weight of the total composition.
9. A composition according to claim 8, wherein the amount of the polymer is from 0.1 to 2% by weight of the total composition.
10. A composition according to any preceding claim, wherein the deflocculating polymer has a specific viscosity less than 0.1 (1g in 100ml methylethylketone at 25°C).
11. A composition according to any preceding claim, having a pH less than 11.
12. A composition according to claim 11, having a pH less than 10.
13. A composition according to any preceding claim, having solid suspending properties.
14. A composition according to any preceding claim, containing solid particles in suspension.
15. A composition according to any preceding claim, which yields less than 0.1% by volume visible phase separation after storage at 25°C for 90 days from the time of preparation.
16. A composition according to any preceding claim, wherein the viscosity of the aqueous continuous phase is less than 25 mPas when measured with a capillary viscometer.
17. A composition according to claim 16, wherein the viscosity of the aqueous continuous phase is less than 10 mPas.
18. A composition according to any preceding claim, comprising at least 20% by weight of detergent active material.
19. A composition according to any preceding claim, comprising at least 30% by weight of detergent active material.
20. A composition according to any preceding claim, having a viscosity of no greater than 2.5 Pas at a shear rate of 21s^{-1} .
21. A composition according to claim 20, having a viscosity of no greater than 1 Pas at a shear rate of 21s^{-1} .

22. A composition according to claim 21, having a viscosity of not greater than 50 mPa.s.
23. A composition according to any preceding claim, which exhibits less phase separation on storage and has a viscosity than an equivalent composition without any of the deflocculating polymers.
24. A composition according to any preceding claim, wherein the volume fraction of the lamellar phase is at least 0.5.
25. A composition according to claim 24, wherein the volume fraction of the lamellar phase is at least 0.6.
26. A composition according to any preceding claim, further comprising from 0.5 to 4.5% by weight of a viscosity reducing polymer which is only partly dissolved in the aqueous continuous phase.
27. A composition according to claim 26, wherein the partly dissolved viscosity reducing polymer comprises a copolymer which includes an alkali metal salt of a polyacrylic, polymethacrylic or maleic acid or anhydride.
28. A composition according to claim 27, having a pH above 8.0.
29. A composition according to any preceding claim, further comprising from 0.05 to 20% of a second polymer which is substantially totally soluble in the aqueous phase and has an electrolyte resistance of more than 5 grams sodium nitrotriacetate in 100ml of a 5% by weight aqueous solution of the polymer, said second polymer also having a vapour pressure in 20% aqueous solution, equal to or less than the vapour pressure of a reference 2% by weight or greater aqueous solution of polyethylene glycol having an average molecular weight of 6000; said second polymer having a molecular weight of at least 1000.
30. A composition according to claim 29, wherein the second polymer has an average molecular weight of at least 2,000.
31. A composition according to one or more of the preceding claims comprising less than 45% by weight of water.
32. Use of a deflocculating polymer having a hydrophilic backbone and at least one hydrophobic side-chain for increasing the stability and reducing the viscosity of a liquid detergent composition comprising a dispersion of lamellar droplets in an aqueous continuous phase.
33. Use of a liquid detergent composition of one or more of the preceding claims in the washing of fabrics.

Patentansprüche

1. Flüssiges Waschmittel, das nach Lagerung bei 25°C für 21 Tage, vom Zeitpunkt der Herstellung an gerechnet, nicht mehr als 2 Volumen-% Phasentrennung ergibt und eine Dispersion lamellarer Tröpfchen in einer wässrigen, kontinuierlichen Phase umfaßt und ebenfalls ein entfloccendes Polymer mit einem hydrophilen Gerüst und mindestens einer hydrophoben Seitenkette umfaßt, mit der Maßgabe, daß
- wenn das Mittel 3 bis 12 % eines Kaliumalkylbenzolsulfonats, 2 bis 8 % einer Kaliumfettsäureseife, 0,5 bis 5 % eines nichtionischen Tensids, 1 bis 25 % Alkalimetalltripolyphosphat, wobei das Alkalimetall Natrium oder Kalium ist und mindestens 50 Gew.-% des Alkalimetalltripolyphosphats Natriumtripolyphosphat sind, gegebenenfalls 20 bis 65 % des Natriumtripolyphosphats durch Tetrakaliumpyrophosphat ersetzt sind und 0,1 bis 2 % eines teilweise veresterten, neutralisierten Copolymers von Maleinsäureanhydrid mit Vinylmethylether, Ethylen oder Styrol umfaßt, wobei alle Prozentangaben auf das Gewicht bezogen sind, das Gewichtsverhältnis des Sulfonats zu der Seife 1:2 bis 6:1 beträgt, das Gewichtsverhältnis des Sulfonats zu dem nichtionischen Tensid 3:5 bis 25:1 beträgt, die Gesamtmenge des Sulfonats, der Seife und des nichtionischen Tensids 7,5 bis 20 Gew.-% beträgt,
- dann das entkoppelnde Polymer nicht allein aus 0,1 bis 2 Gew.-% eines teilweise veresterten, neutralisierten Copolymers von Maleinsäureanhydrid mit Vinylmethylether, Ethylen oder Styrol besteht;
- und mit der weiteren Maßgabe, daß
- wenn das Mittel Seife, Tetrakaliumpyrophosphat und zwitterionisches Tensid umfaßt,
- dann das entkoppelnde Polymer nicht allein aus einem Copolymer von Methylvinylether und Maleinsäureanhydrid, verestert mit dem zwitterionischen Tensid, besteht.

Formel (I) aufweist



worin:

z 1 ist; (x + y) : z 4:1 bis 1000:1 ist; wobei die Monomereinheiten in zufälliger Reihenfolge vorliegen können; y 0 bis zu einem Maximum gleich dem Wert von x ist und n mindestens 1 ist;

R¹ -CO-O-, -O-, -O-CO-, -CH₂-, -CO-NH- wiedergibt oder nicht vorliegt;

R² 1 bis 50 unabhängig ausgewählte Alkylenoxygruppen wiedergibt oder nicht vorliegt, mit der Maßgabe, daß, wenn R³ nicht vorliegt und R⁴ Wasserstoff wiedergibt oder nicht mehr als 4 Kohlenstoffatome enthält, dann R² eine Alkylenoxygruppe mit mindestens 3 Kohlenstoffatomen enthalten muß;

R³ eine Phenylbindung wiedergibt oder nicht vorliegt;

R⁴ Wasserstoff oder eine C₁₋₂₄-Alkyl- oder C₂₋₂₄-Alkenylgruppe wiedergibt, mit den Maßgaben, daß,

a) wenn R¹ -O-CO- wiedergibt, R² und R³ nicht vorliegen dürfen und R⁴ mindestens 5 Kohlenstoffatome enthalten muß;

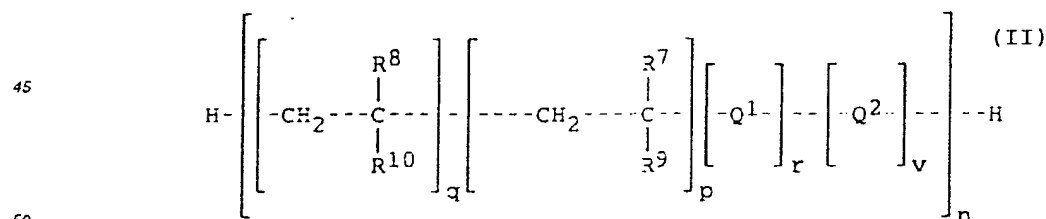
b) wenn R² nicht vorliegt, R⁴ kein Wasserstoffatom ist und wenn R³ nicht vorliegt, dann R⁴ mindestens 5 Kohlenstoffatome enthalten muß;

R⁵ Wasserstoff oder eine Gruppe der Formel -COOA⁴ bedeutet;

R⁶ Wasserstoff oder C₁₋₄-Alkyl darstellt; und

A¹, A², A³ und A⁴ unabhängig voneinander ausgewählt sind aus Wasserstoff, Alkalimetallen, Erdalkalimetallen, Ammonium- und Aminbasen und C₁₋₄ Alkyl

oder der Formel (II):



worin:

Q² eine Moleküleinheit der Formel (IIa) wiedergibt:



(IIa)

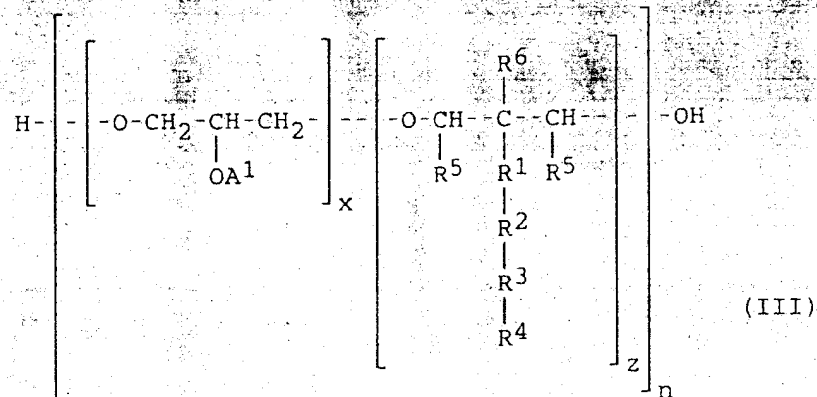
worin z und R^{1-6} wie für Formel (I) definiert sind, A^1 wie für Formel (I) definiert sind oder $-\text{CH}(\text{OH})-$ sind, wobei 1 bis 50 beträgt und wobei die Monomereinheiten in zufälliger Ordnung vorliegen können, Q^1 ein multifunktionelles Monomer ist, das das Verzweigen des Polymers erlaubt, wobei die Monomere des Polymers an Q^1 in beliebiger Richtung und beliebiger Ordnung gebunden sein können, wodurch sich gegebenenfalls ein verzweigtes Polymer ergibt,

n und z wie vorstehend definiert sind, $v = 1$, und $(x + y + p + q + z)$ bis 1000 beträgt, wobei die Monomereinheiten in zufälliger Weise angeordnet sein können,

R^7 und R^8 , CH_3 oder $-\text{H}$ darstellen,

R^9 und R^{10} unabhängig voneinander Gruppen bedeuten aus: $-\text{SO}_3\text{Na}$, $-\text{CO}-\text{O}-\text{C}_2\text{H}_4$, $-\text{OSO}_3\text{Na}$, $-\text{CO}-\text{O}-\text{NH}-\text{C}(\text{CH}_3)_2-\text{SO}_3\text{Na}$, $-\text{CO}-\text{NH}_2$, $-\text{O}-\text{CO}-\text{CH}_3$, $-\text{OH}$.

3. Mittel nach Anspruch 1 oder 2, wobei das Polymer die Formel III aufweist:



worin:

x 4 bis 1000 ist, n , z und R^{1-6} wie in Formel I definiert sind, wobei die Monomereinheiten in zufälliger Ordnung vorliegen können,

A^1 wie vorstehend für Formel I definiert ist oder $-\text{CO}-\text{CH}_2-\text{C}(\text{OH})-\text{CO}_2\text{A}^1-\text{CH}_2-\text{CO}_2\text{A}^1$ ist oder ein Verzweigungspunkt sein kann, an den weitere Moleküle der Formel (III) gebunden sind.

4. Mittel nach Anspruch 1, wobei das Polymer die Formel (IV) aufweist

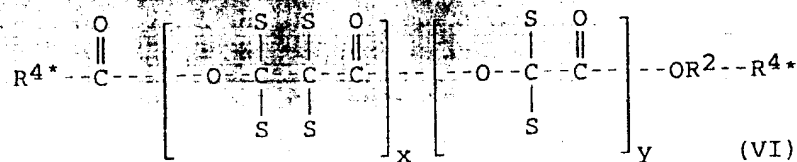


R^{12} -OH, -CH₂OH, -CH₂OSO₃A¹, COOA¹, -CH₂-OCH₃ wiedergibt:

$$\text{HO} - \left[\begin{array}{c} \text{CHOH} - \text{CHOH} \\ \diagup \quad \diagdown \\ -\text{CH} \quad \text{HC-O} \\ \diagdown \quad \diagup \\ \text{CH} - \text{O} \\ | \\ \text{CH}_2\text{OR}^2\text{H} \end{array} \right]_x - \left[\begin{array}{c} \text{CH}_2\text{OR}^2\text{H} \\ | \\ \text{CH} - \text{O} \\ \diagdown \quad \diagup \\ -\text{CH} \quad \text{HC-O} \\ \diagup \quad \diagdown \\ \text{CHOH} - \text{CH} \\ | \\ \text{R}^1 \\ | \\ \text{R}^2 \\ | \\ \text{R}^3 \\ | \\ \text{R}^4 \end{array} \right]_z - \text{H} \quad (V)$$

z, n und R^{1-6} wie vorstehend für Formel I definiert sind und x wie für Formel III definiert ist.

5. Mittel nach Anspruch 1, wobei das Polymer die Formel VI aufweist:



worin:

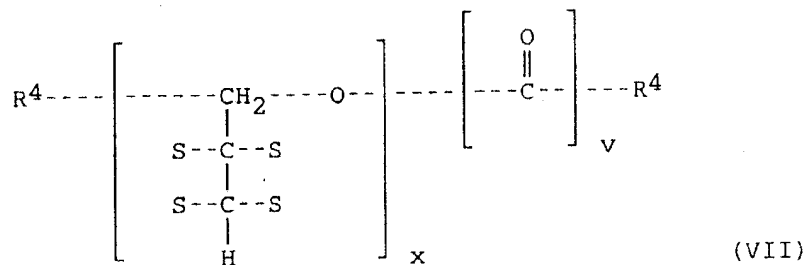
wenn z die Gesamtzahl an R^4 -Gruppen wiedergibt, dann das Verhältnis $(x+y):z$ 4:1 bis 1000:1 beträgt; R^4 R^4 oder -H ist,

R^2 und R^4 wie vorstehend für Formel I definiert sind

und S ausgewählt ist aus -H, $-\text{COOA}^1$, $-\text{CH}_2\text{COOA}^1$, $-\text{CH}(\text{COOA}^1)_2$, $(\text{CH}_2\text{COOA}^1)_2\text{H}$, wobei A^1 wie für Formel I definiert ist oder R^4 ist;

mit der Maßgabe, daß mindestens eine Gruppe R^4 als Seitenkette vorliegt;

oder der Formel (VII):



worin:

x, z, S und R^4 wie vorstehend für Formel VI definiert sind;

und wobei mindestens eine Gruppe R^4 als Seitenkette vorliegt; v 0 oder 1 ist.

6. Mittel nach einem oder mehreren der vorangehenden Ansprüche, wobei das mittlere Molekulargewicht des Polymers 500 bis 500 000, bestimmt durch Gelpermeationschromatographie unter Verwendung von Polyacrylatstandards, beträgt.
7. Mittel nach Anspruch 6, wobei das mittlere Molekulargewicht 1000 bis 30 000 beträgt.
8. Mittel nach einem vorangehenden Anspruch, wobei die Gesamtmenge an entflokkendem Polymer 0,01 bis 5 Gew.-% des gesamten Mittels beträgt.
9. Mittel nach Anspruch 8, wobei die Menge des Polymers 0,1 bis 2 Gew.-% des gesamten Mittels beträgt.
10. Mittel nach einem vorangehenden Anspruch, wobei das entflokkende Polymer eine spezifische Viskosität von weniger als 0,1 (1 g in 100 ml Methylethylketon bei 25°C) aufweist.
11. Mittel nach einem vorangehenden Anspruch mit einem pH-Wert geringer als 11.
12. Mittel nach Anspruch 11 mit einem pH-Wert geringer als 10.
13. Mittel nach einem vorangehenden Anspruch mit Feststoff suspendierenden Eigenschaften.
14. Mittel nach einem vorangehenden Anspruch, das feste Teilchen in Suspension enthält.

17. Mittel nach Anspruch 16, wobei die Viskosität bei einer Schergeschwindigkeit von nicht mehr als 10 mPa s beträgt.
18. Mittel nach einem vorangehenden Anspruch, umfassend mindestens 20 Gew.-% Waschmittelaktivstoff.
19. Mittel nach einem vorangehenden Anspruch, umfassend mindestens 40 Gew.-% Waschmittelaktivstoff.
20. Mittel nach einem vorangehenden Anspruch mit einer Viskosität von nicht mehr als 2,5 Pa s bei einer Schergeschwindigkeit von 21 s⁻¹.
21. Mittel nach Anspruch 20 mit einer Viskosität von nicht mehr als 1 Pa s bei einer Schergeschwindigkeit von 21 s⁻¹.
22. Mittel nach Anspruch 21 mit einer Viskosität von nicht mehr als 750 mPa s bei einer Schergeschwindigkeit von 21 s⁻¹.
23. Mittel nach einem vorangehenden Anspruch, das nach Lagerung wenig Phasentrennung aufweist und eine geringere Viskosität aufweist als ein äquivalentes Mittel ohne das Entflockungspolymer.
24. Mittel nach einem vorangehenden Anspruch, wobei die Volumenfraktion der lamellaren Phase mindestens 0,5 beträgt.
25. Mittel nach Anspruch 24, wobei die Volumenfraktion der lamellaren Phase mindestens 0,6 beträgt.
26. Mittel nach einem vorangehenden Anspruch, zusätzlich 0,5 bis 4,5 Gew.-% eines die Viskosität vermindernenden Polymers enthaltend, das nur teilweise in der wässrigen, kontinuierlichen Phase gelöst ist.
27. Mittel nach Anspruch 26, wobei das teilweise gelöste, die Viskosität vermindernde Polymer ein Copolymer umfaßt, das ein Alkalimetallsalz einer Polyacryl-, Polymethacryl- oder Maleinsäure oder -anhydrid umfaßt.
28. Mittel nach Anspruch 27 mit einem pH oberhalb 8,0.
29. Mittel nach einem vorangehenden Anspruch, zusätzlich 0,05 bis 20 % eines zweiten Polymers umfassend, das im wesentlichen vollständig in der wässrigen Phase löslich ist und das eine Elektrolytbeständigkeit von mehr als 5 g Natriumnitritotriacetat in 100 ml einer wässrigen, 5 gewichtsprozentigen Lösung des Polymers aufweist, wobei das zweite Polymer ebenfalls einen Dampfdruck in 20 %-iger wässriger Lösung gleich oder geringer als der Dampfdruck eines Bezugs einer 2- oder mehr gewichtsprozentigen wässrigen Lösung von Polyethylenglycol mit einem mittleren Molekulargewicht von 6000 aufweist, wobei das zweite Polymer ein Molekulargewicht von mindestens 1000 aufweist.
30. Mittel nach Anspruch 29, wobei das zweite Polymer ein mittleres Molekulargewicht von mindestens 2000 aufweist.
31. Mittel nach einem oder mehreren der vorangehenden Ansprüche, umfassend weniger als 45 Gew.-% Wasser.
32. Verwendung eines entflockenden Polymers mit einem hydrophilen Gerüst und mindestens einer hydrophoben Seitenkette zur Erhöhung der Stabilität und Verminderung der Viskosität eines flüssigen Waschmittels, umfassend eine Dispersion von lamellaren Tröpfchen in einer wässrigen, kontinuierlichen Phase.
33. Verwendung eines flüssigen Waschmittels nach einem oder mehreren der vorangehenden Ansprüche zum Waschen von Textilien.

est un produit homogénéisé qui ne donne pas plus de 2% en volume de séparation de phase lorsqu'on la laisse reposer à température ambiante à partir du moment de sa préparation et qui comprend une dispersion de gouttelettes lamellaires dans une phase aqueuse continue, et qui comprend également un polymère défloculant ayant un squelette hydrophile et au moins une chaîne latérale hydrophobe, à condition que

quand la composition comprend entre 3 % et 12 % d'un alkylbenzènesulfonate de potassium, entre 2 et 8 % d'un savon d'acide gras potassique, entre 0,5 et 5 % d'un agent tensioactif non ionique, entre 1 et 25 % d'un tripolyphosphate de métal alcalin, dans lequel le métal alcalin est du sodium ou du potassium, et au moins 50 % en poids du tripolyphosphate de métal alcalin est du tripolyphosphate de sodium, 20 à 65 % du tripolyphosphate de sodium étant éventuellement remplacés par du pyrophosphate tétrapotassique, et entre 0,1 et 2 % d'un copolymère neutralisé partiellement estérifié d'anhydride maléique avec de l'éther vinylméthylque, de l'éthylène ou du styrène, tous les pourcentage étant en poids, le rapport pondéral dudit sulfonate audit savon étant compris entre 1/2 et 6/1, le rapport pondéral dudit sulfonate audit agent tensioactif non ionique étant compris entre 3/5 et 25/1, la quantité totale desdits sulfonate, savon et agent tensioactif non ionique étant comprise entre 7,5 et 20 % en poids,

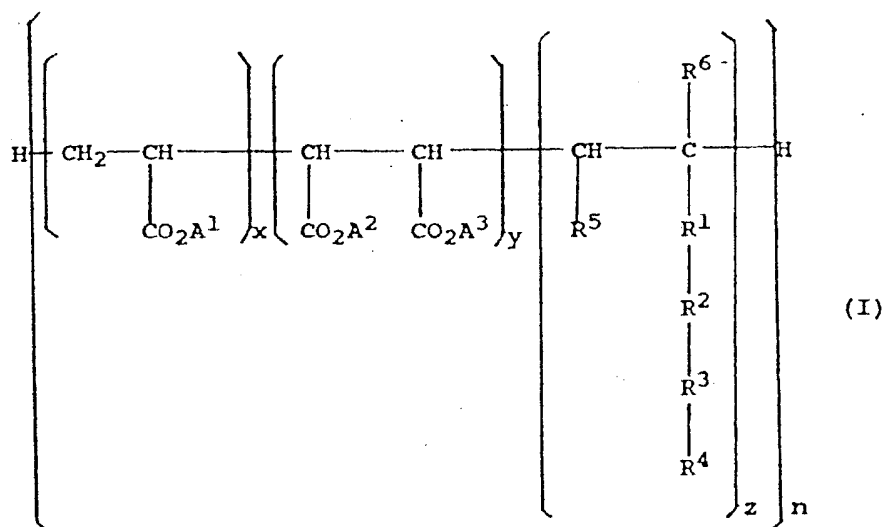
alors le polymère de découplage n'est pas uniquement constitué de 0,1 % à 2 % en poids d'un copolymère neutralisé partiellement estérifié d'anhydride maléique avec de l'éther vinylnméthylque, de l'éthylène ou du styrène :

et à condition supplémentaire que

et à condition supplémentaire que
quand la composition comprend un savon, du pyrophosphate tétrapotassique et un agent tensioactif switterionique,

alors le polymère de découplage n'est pas uniquement constitué d'un interpolymère d'éther méthylvinyle et d'anhydride maléique estérifié avec l'agent tensioactif switterionique.

2. Composition selon la revendication 1, dans laquelle le polymère répond à la formule générale (I)



dans laquelle

z vaut 1; $(x + y)/z$ est compris entre $4/1$ et $1000/1$; dans laquelle les motifs monomères peuvent être en ordre aléatoire; y étant compris entre 0 et un maximum égal à la valeur de x; et n vaut au moins 1;

B¹ représente -CO-O-, -O-, -O-CO-, CH₂-, -CO-NH- ou est absent ;

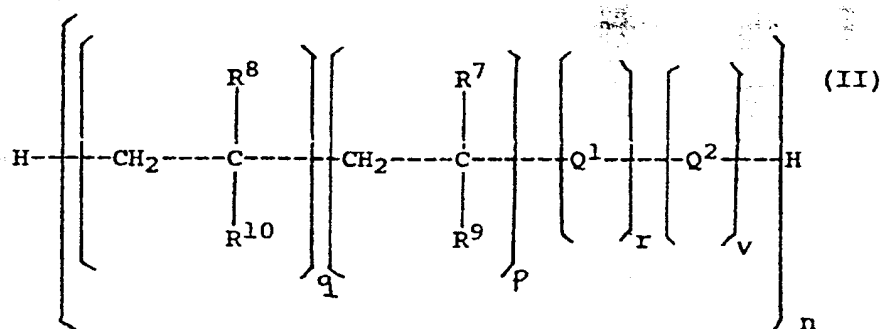
alors R² doit contenir un groupe alkylénoxy avec au moins 3 atomes de carbone ;

représente un atome d'hydrogène ou un groupe alkyle en C_{1-4} ou un groupe alkoyle en C_{1-4} , ou est absent ;
 R¹⁰ représente un atome d'hydrogène ou un groupe alkyle en C_{1-4} ou un groupe alkoyle en C_{1-4} , ou est absent ;
 conditions selon lesquelles :

- a) lorsque R¹ représente -O-CO-, R² et R³ doivent être absent et R⁴ doit contenir au moins 5 atomes de carbone ;
 b) lorsque R² est absent, R⁴ n'est pas un atome d'hydrogène et lorsque R³ est absent, alors R⁴ doit contenir au moins 5 atomes de carbone ;

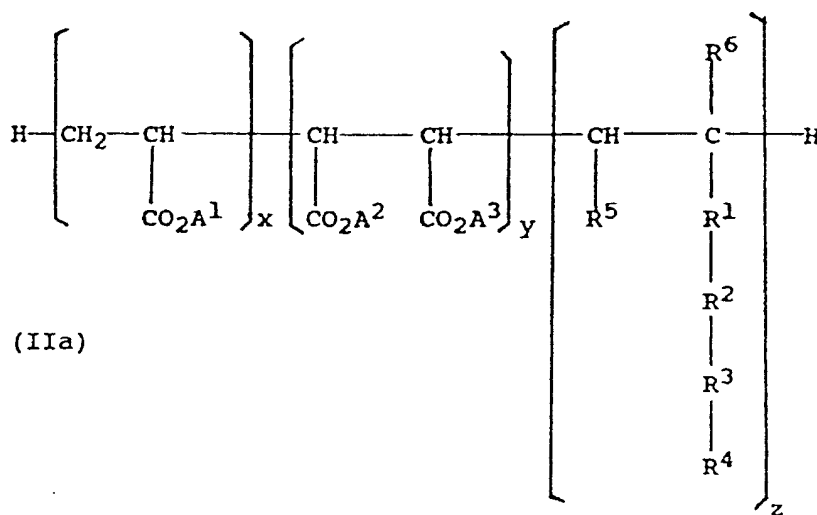
R⁵ un atome d'hydrogène ou un groupe de formule -COOA⁴ ;
 R⁶ représente un atome d'hydrogène ou un groupe alkyle C_{1-4} et
 A¹, A², A³ et A⁴ sont indépendamment choisis parmi un atome d'hydrogène, des métaux alcalins, des métaux alcalino-terreux, des bases d'ammonium et amine et un groupe alkyle C_{1-4}

ou à la formule (II) :



dans laquelle :

Q² est une entité moléculaire de formule (IIa) :



dans laquelle z et R¹⁻⁶ sont tels que définis pour la formule (I); A¹⁻⁴ sont tels que définis pour la formule (I) ou

représentent $(C_2H_4O)_n$ dans lequel n est compris entre 1 et 50, tel dans lequel les motifs monomères peuvent être en ordre aléatoire ;

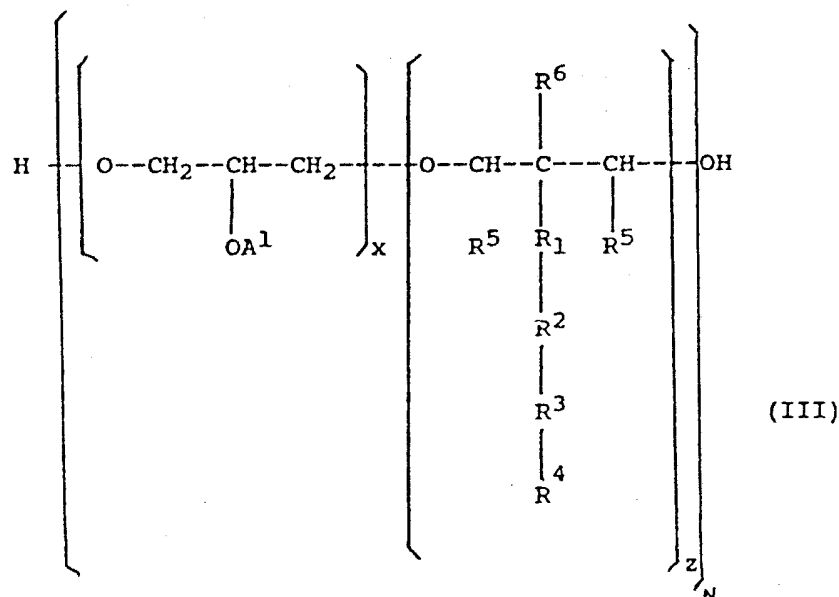
Q^1 est un monomère multifonctionnel, permettant la ramification du polymère, dans lequel les monomères du polymère peuvent être reliés à Q^1 dans toutes les directions, dans un ordre quelconque, ce qui peut résulter en un polymère ramifié ;

n et z sont tels que définis ci-dessus ; $v = 1$ et $(x + y + p + q + r)/z$ est compris entre $4/1$ et $1000/1$, dans lequel les motifs monomères peuvent être en ordre aléatoire ;

R^7 et R^8 représentent $-CH_3$ ou $-H$;

R^9 et R^{10} représentent des groupes indépendamment choisis parmi $-SO_3Na$, $-COO-C_2H_4-OSO_3Na$, $-CO-O-NH-C(CH_3)_2-SO_3Na$, $-CO-NH_2$, $-O-CO-CH_3$, $-OH$;

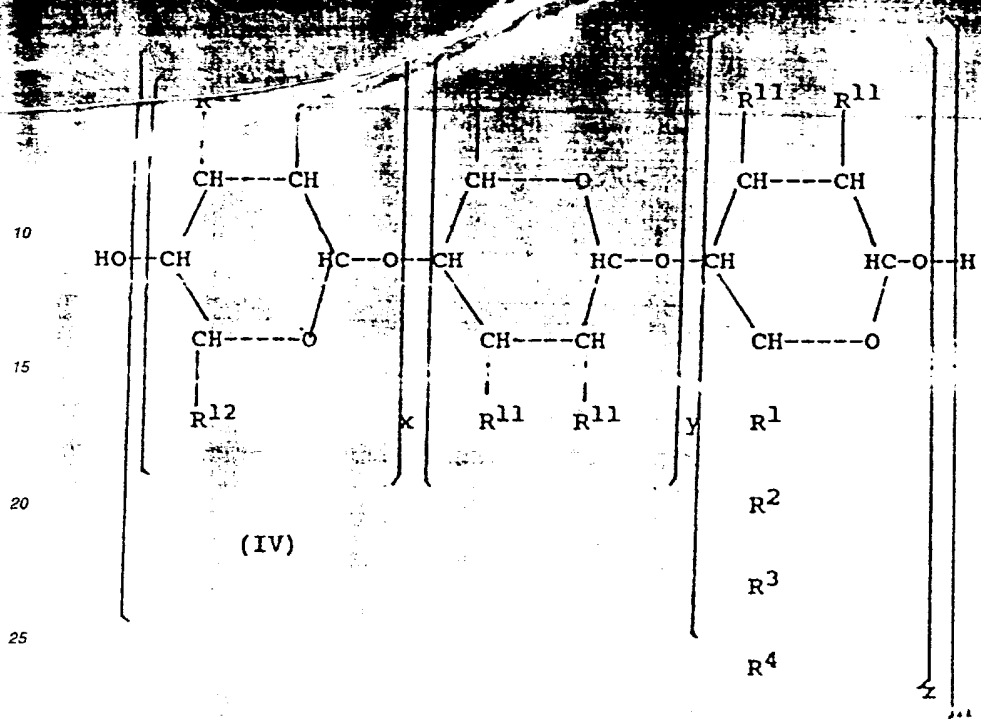
3. Composition selon la revendication 1 ou la revendication 2, dans laquelle le polymère répond à la formule III :



dans laquelle x est compris entre 4 et 1000 et z et R^1-6 sont tels que définis pour la formule (I), dans lequel les motifs monomères peuvent être en ordre aléatoire ;

A^1 est tel que défini pour la formule I ou représente $-CO-CH_2-C(OH)-CO_2A^1-CH_2-CO_2A^1$, ou peut être un point de ramification auquel d'autres molécules de formule (III) sont attachées.

4. Composition selon la revendication 1, dans laquelle le polymère répond à la formule (IV)



dans laquelle :

z, n et A¹ sont tels que définis pour la formule I ; (x + y)/z est compris entre 4/1 et 1000/1, dans laquelle les monomères peuvent être en ordre aléatoire.

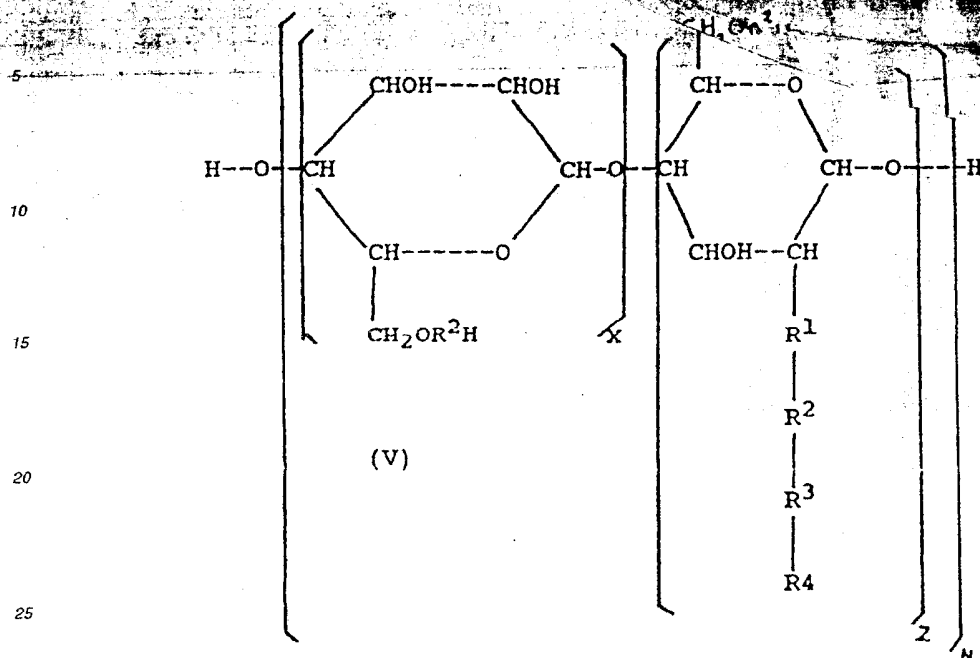
R¹ est tel que défini ci-dessous pour la formule I ou peut représenter -CH₂-O-, -CH₂-C(=O)-O-, -NH-CO-

R², R³ et R⁴ sont tels que définis ci-dessous pour la formule I ;

R¹¹ représente -OH, -NH-CO-CH₃, ou -OSO₃A¹ ;

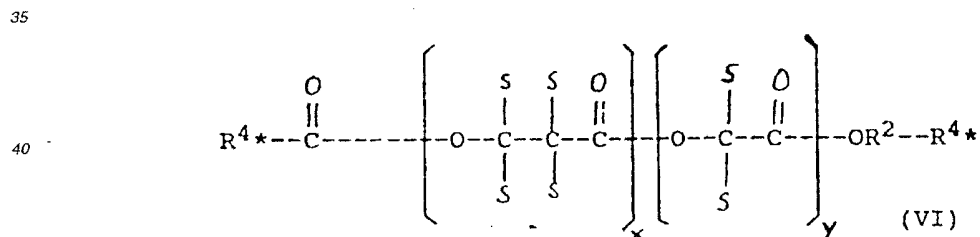
R¹² représente -OH, -CH₂OH, CH₂OSO₃A¹, COOA¹, -CH₂-C(=O)-CH₃ ;

ou à la formule (V) :



30 dans laquelle :
 z, n et R¹⁻⁶ sont tels que définis ci-dessus pour la formule I, et x est tel que défini pour la formule III.

5. Composition selon la revendication 1, dans laquelle le polymère répond à la formule VI :

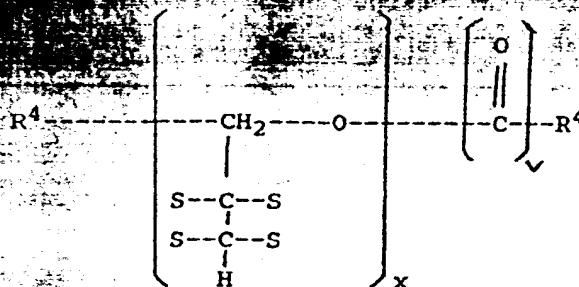


45 dans laquelle :

si z est la somme des groupes R⁴, alors le rapport (x + y)/z est compris entre 4/1 et 1000/1, R⁴ représente R⁴ ou -H.

50 R² et R⁴ sont tels que définis ci-dessus pour la formule I;
 et S est choisi parmi -H, COOA¹, -CH₂COOA¹, -CH(COOA¹)₂, (CH₂COOA¹)₂H, dans lequel A¹ est tel que défini pour la formule I ou représente R⁴ ;
 à la condition qu'au moins un groupe R⁴ soit présent en tant que chaîne latérale ;

55 ou à la formule (VII) :



(VII)

dans laquelle :

x, z, s et R⁴ sont tels que définis ci-dessus pour la formule VI;

et dans laquelle au moins un groupe R⁴ est présent en tant que chaîne latérale ; v vaut 0 ou 1.

6. Composition selon une ou plusieurs des revendications précédentes, dans laquelle le poids moléculaire moyen du polymère est compris entre 500 et 500 000 selon une détermination par chromatographie de perméation sur gel, en utilisant des étalons de polyacrylate.
7. Composition selon la revendication 6, dans laquelle ledit poids moléculaire moyen est compris entre 1000 et 30 000.
8. Composition selon l'une quelconque des revendications précédentes, dans laquelle la quantité totale de polymère défloculant est comprise entre 0,01 et 5 % en poids de la composition totale.
9. Composition selon la revendication 8, dans laquelle la quantité de polymère est comprise entre 0,1 et 2 % en poids de la composition totale.
10. Composition selon l'une quelconque des revendications précédentes, dans laquelle le polymère défloculant a une viscosité spécifique inférieure à 0,1 (1 g dans 100 ml de méthyléthylcétone à 25°C).
11. Composition selon l'une quelconque des revendications précédentes, dont le pH est inférieur à 11.
12. Composition selon la revendication 11, dont le pH est inférieur à 10.
13. Composition selon l'une quelconque des revendications précédentes, ayant des propriétés de suspension des solides.
14. Composition selon l'une quelconque des revendications précédentes, contenant des particules solides en suspension.
15. Composition selon l'une quelconque des revendications précédentes, qui donne moins de 0,1 % en volume de séparation de phase visible après stockage à 25°C pendant 90 jours à partir du moment de la préparation.
16. Composition selon l'une quelconque des revendications précédentes, dans laquelle la viscosité de la phase aqueuse continue est inférieure à 25 mPas lorsqu'on la mesure avec un viscomètre capillaire.
17. Composition selon la revendication 16, dans laquelle la viscosité de la phase aqueuse continue est inférieure à 10 mPas.
18. Composition selon l'une quelconque des revendications précédentes, comprenant au moins 20 % en poids de matériau détergent actif.
19. Composition selon l'une quelconque des revendications précédentes, comprenant au moins 30 % en poids de matériau détergent actif.

20. Composition selon l'une quelconque des revendications précédentes, dont la viscosité est inférieure à 25 mPas à un taux de cisaillement de 21 s^{-1} .

21. Composition selon la revendication 20, dont la viscosité est inférieure à 25 mPas à un taux de cisaillement de 21 s^{-1} .

22. Composition selon la revendication 21, dont la viscosité est inférieure à 750 mPas à un taux de cisaillement de 21 s^{-1} .

23. Composition selon l'une quelconque des revendications précédentes, qui présente dont la séparation de phase en stockage est moindre et dont la viscosité est plus faible que celles d'une composition équivalente dépourvue de tout polymère défloculant.

24. Composition selon l'une quelconque des revendications précédentes, dans laquelle la fraction volumique de la phase lamellaire est d'au moins 0,5.

25. Composition selon la revendication 24, dans laquelle la fraction volumique est d'au moins 0,6.

26. Composition selon l'une quelconque des revendications précédentes, comprenant en outre entre 0,5 et 4,5 % en poids d'un polymère réduisant la viscosité qui ne se dissout que partiellement dans la phase aqueuse continue.

27. Composition selon la revendication 26, dans laquelle le polymère réduisant la viscosité partiellement dissous est constitué d'un copolymère qui comprend un sel de métal alcalin d'un acide ou d'un anhydride polyacrylique, polyméthacrylique ou maléique.

28. Composition selon la revendication 27, ayant un pH supérieur à 8,0.

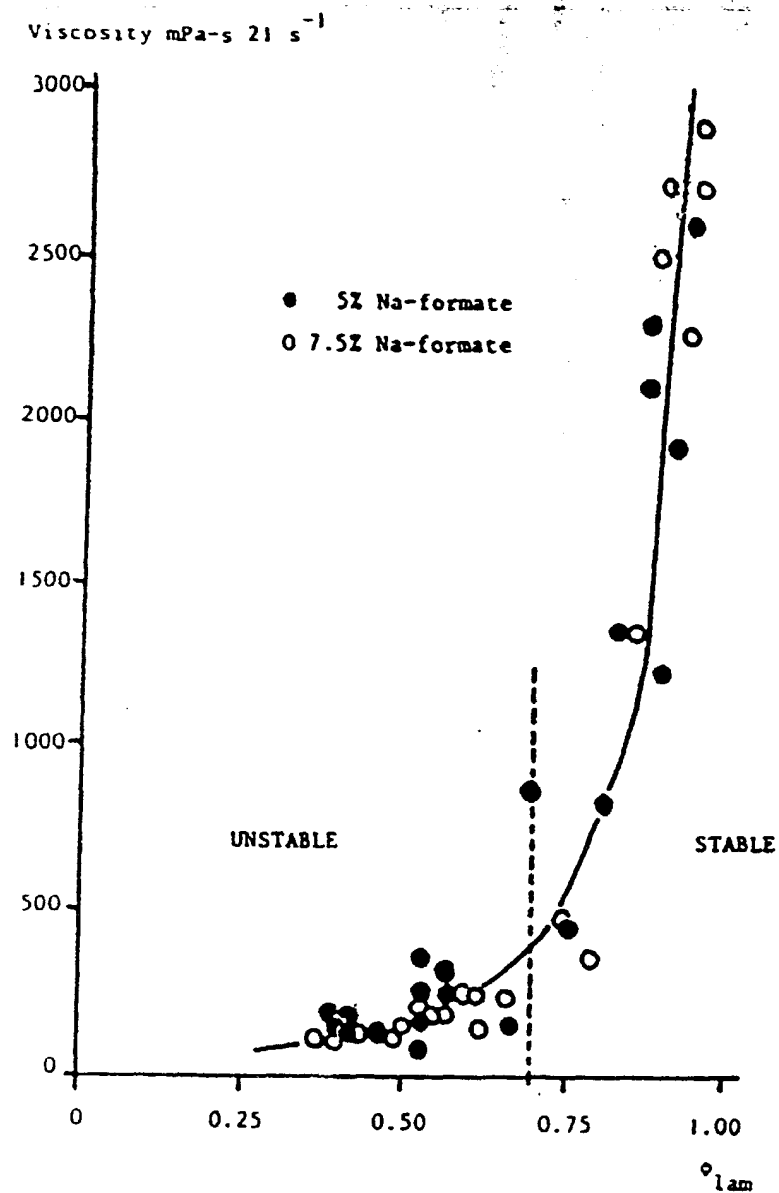
29. Composition selon l'une quelconque des revendications précédentes, comprenant en outre entre 0,05 et 20 % d'un second polymère qui est pratiquement totalement soluble dans la phase aqueuse et qui a une résistance électrolytique supérieure à 5 grammes de nitrilotriacétate de sodium dans 100 ml d'une solution à 5 % en poids du polymère, ledit second polymère ayant également une pression de vapeur en solution aqueuse à 20 % égale ou inférieure à la pression de vapeur d'une solution aqueuse de référence à 2 % ou plus en poids de polyéthylène-glycol de poids moléculaire moyen de 6000 ; ledit second polymère ayant un poids moléculaire d'au moins 1000.

30. Composition selon la revendication 29, dans laquelle le second polymère a un poids moléculaire moyen d'au moins 2000.

31. Composition selon une ou plusieurs des revendications précédentes comprenant moins de 45 % en poids d'eau.

32. Utilisation d'un polymère défloculant ayant un squelette hydrophile et au moins une chaîne latérale hydrophobe pour augmenter la stabilité et réduire la viscosité d'une composition détergente liquide comprenant une dispersion de gouttelettes lamellaires dans une phase aqueuse continue.

33. Utilisation d'une composition détergente liquide d'une ou plusieurs des revendications précédentes pour le lavage de tissus.

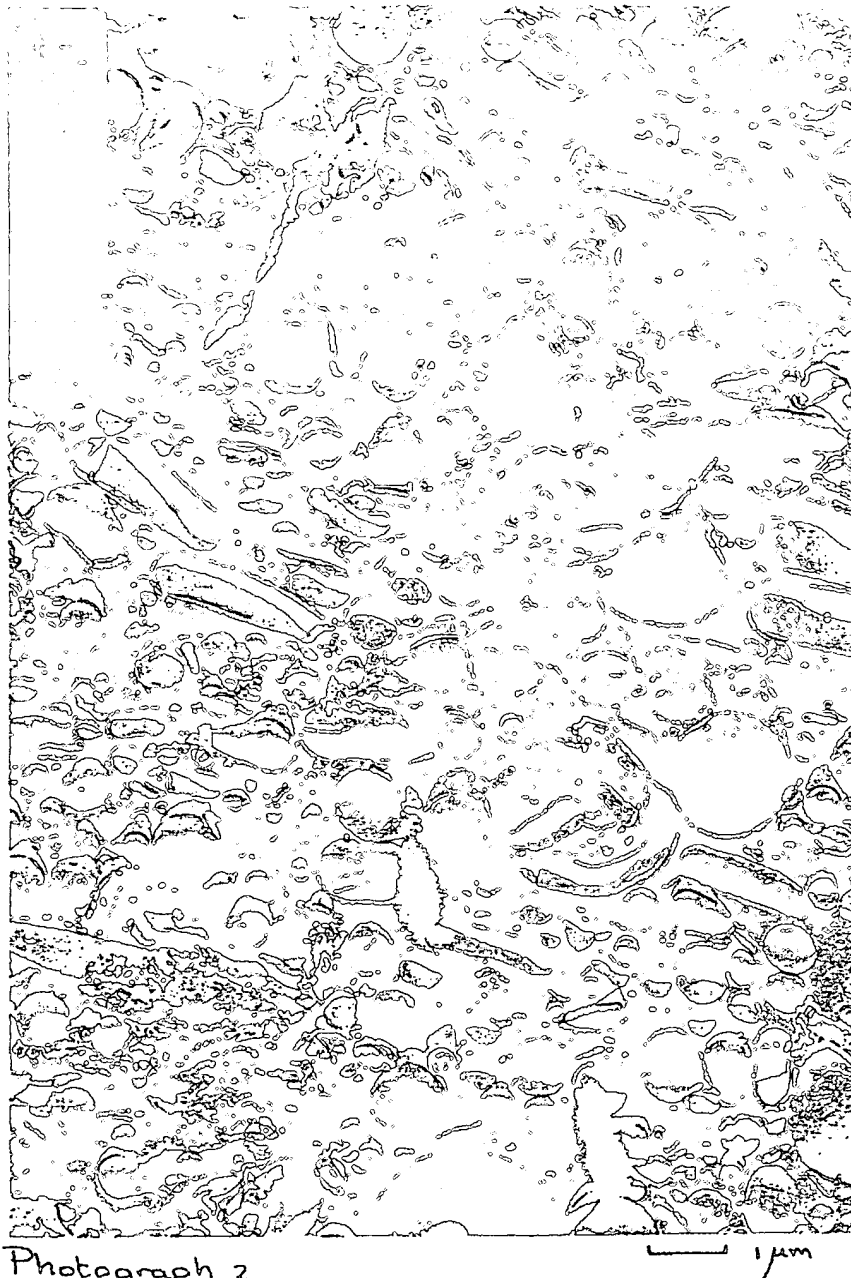


Relation between the viscosity and the volume fraction lamellar phase ϕ_{lam} .



Photograph 1

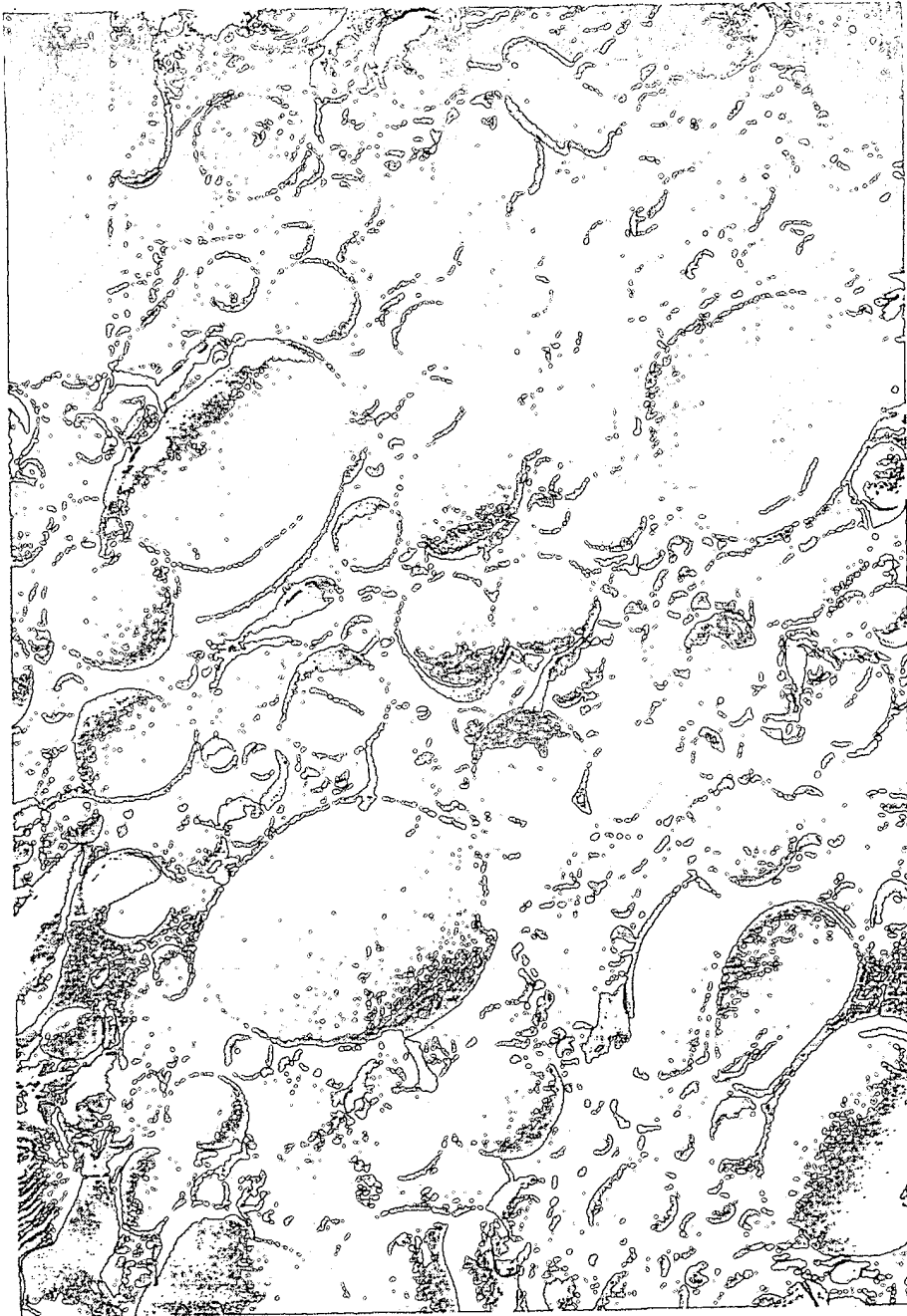
EM-micrograph of part of a floc of lamellar droplets, i.e. the droplets are strongly flocculated. Part of the continuous electrolyte phase is visible.
Basic formulation 1 without 'deflocculating' polymer



Photograph 2

EM-micrograph of basic formulation 1,
with 1% of 'deflocculating' polymer A-2.

The individual character of the droplets,
i.e. the 'deflocculating' effect of the polymer,
is beautifully demonstrated. Compare with Photo 1

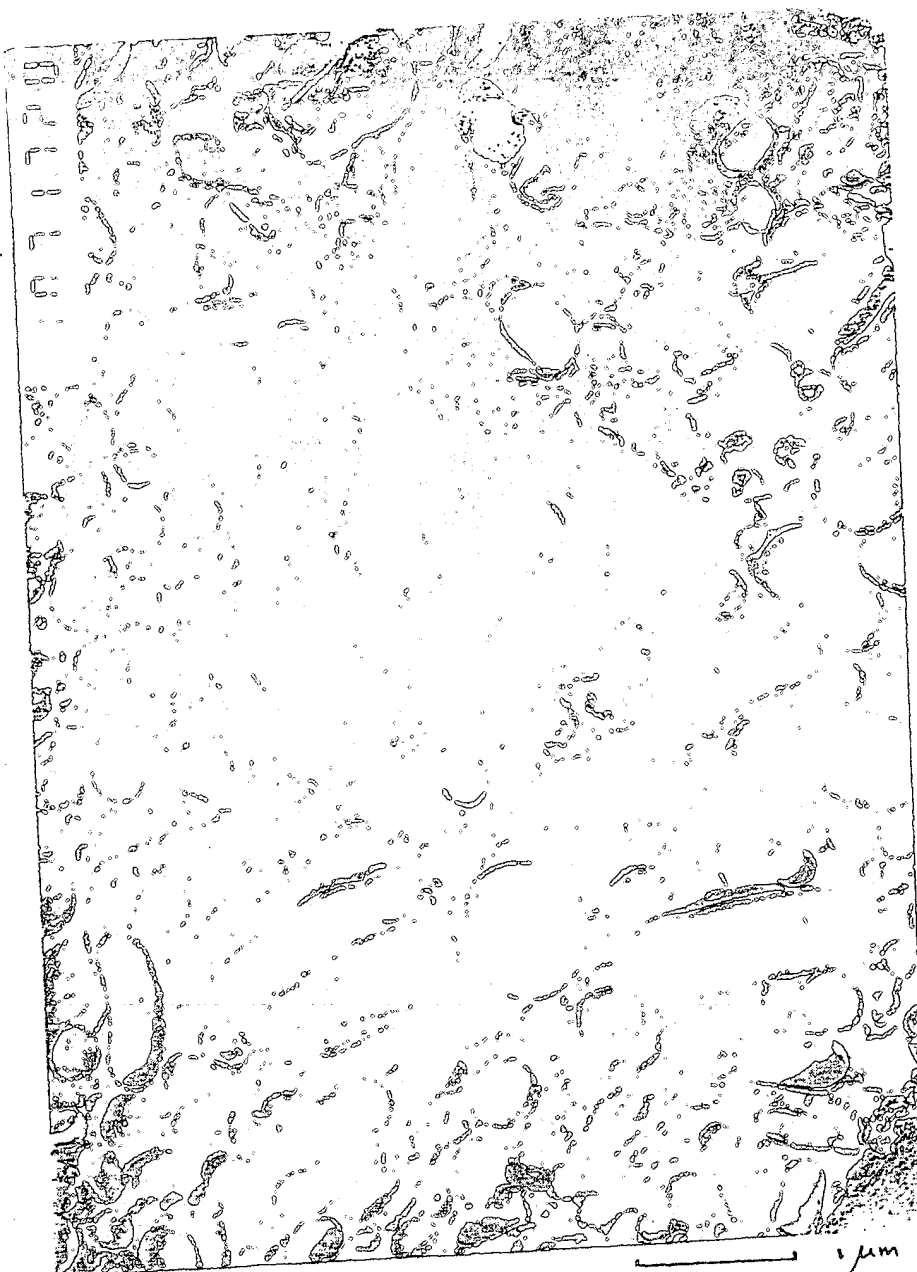


Photograph 3
As Photograph 2, but with 0.5% deflocculating polymer A-5



Photograph 4

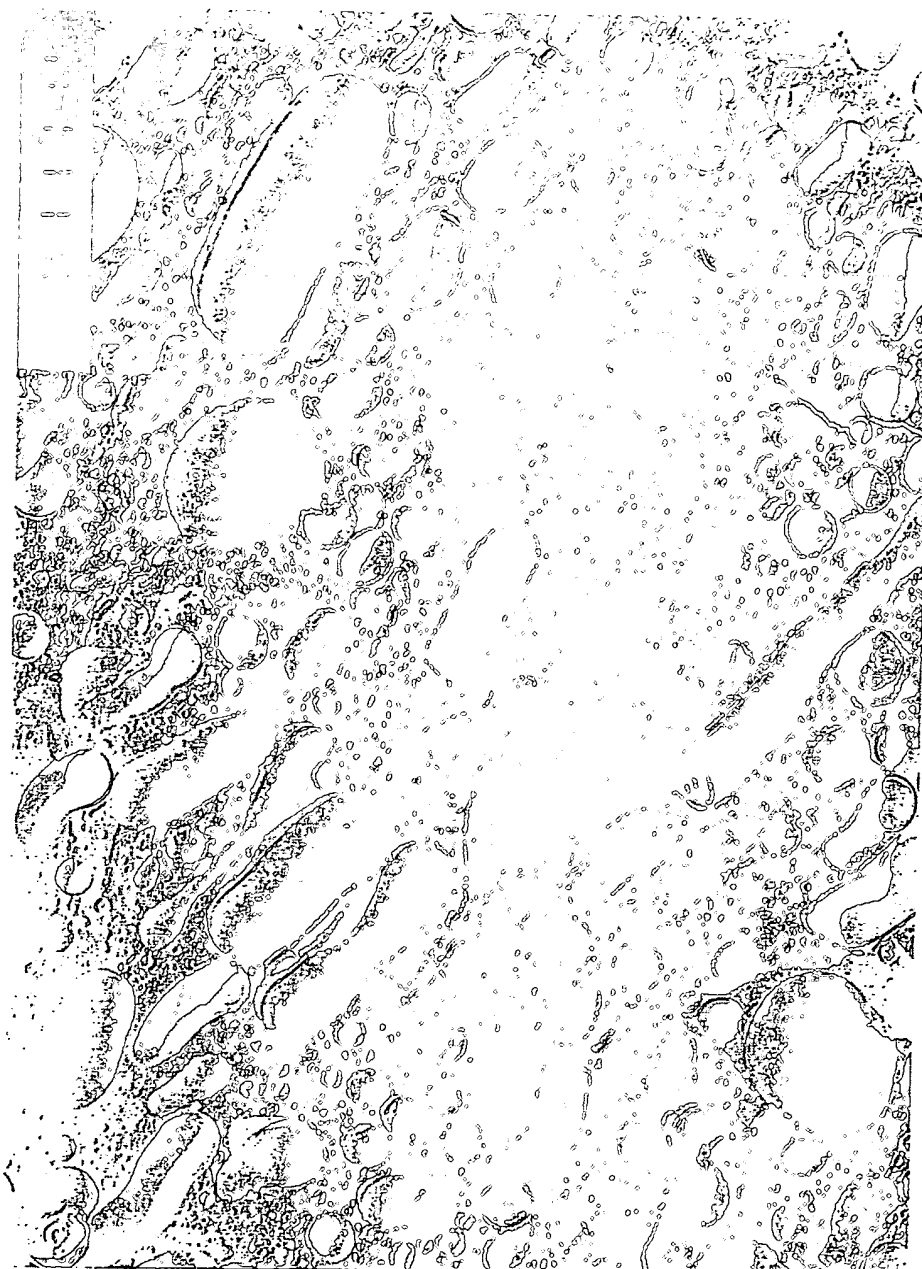
EM-micro graph of part of a floc of lamellar droplets, i.e. the droplets are strongly flocculated. The continuous electrolyte phase is not visible. Basic formulation 2 without 'deflocculating' polymer



Photograph 5

EM-micrograph of basic formulation 2, with 2% of 'deflocculating' polymer A-7.

The individual character of the droplets, i.e. the 'deflocculating' effect of the polymer, is beautifully demonstrated. Compare with Photograph 4



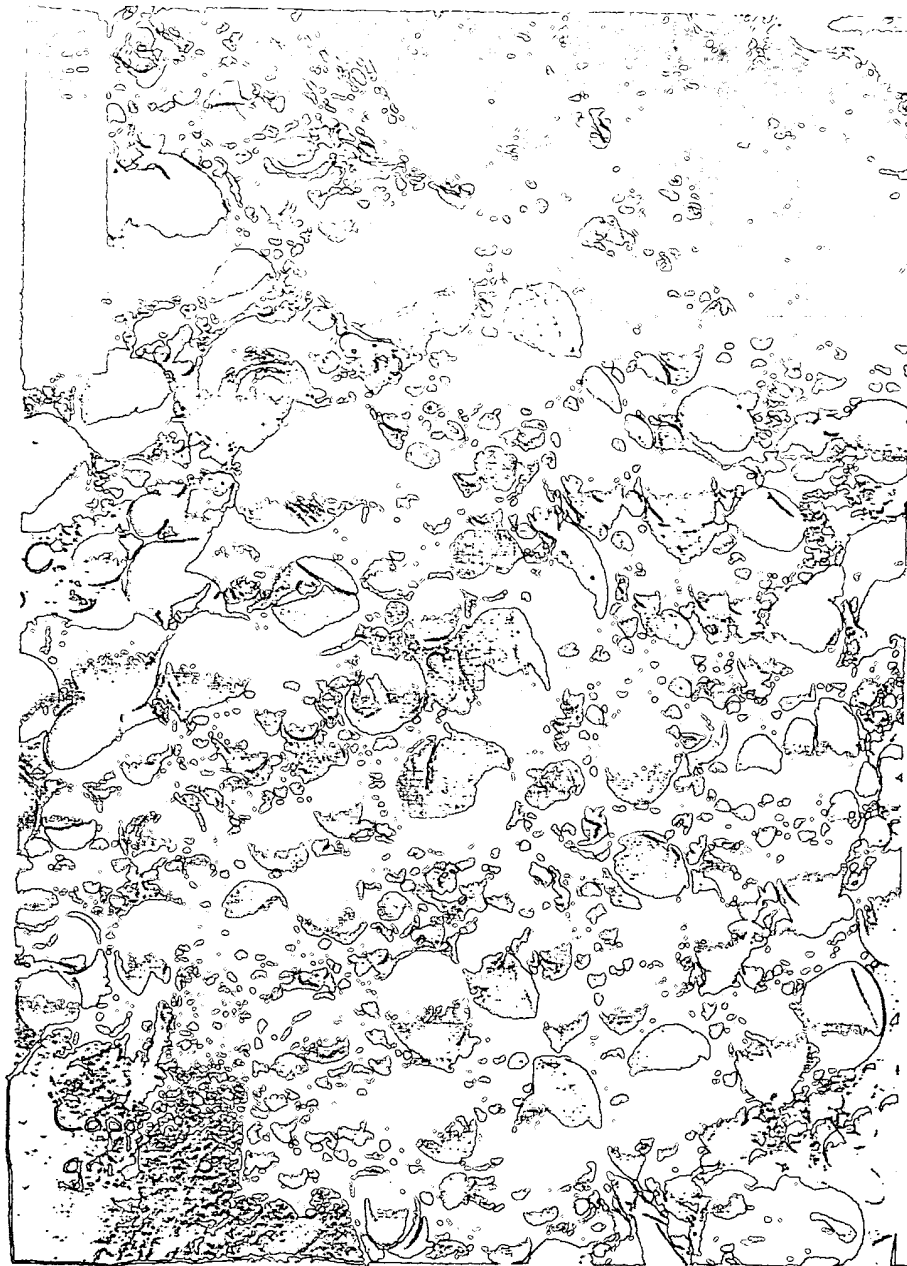
Photograph 6
 As Photograph 5, but with 'deflocculating' polymer A-11



Photo graph 7

EM- micrograph of basic formulation 49 without 'deflocculating' polymer. The flocculation of the lamellar droplets can be detected in two ways:

- flocculation as such (A)



Photograph 8

EM-micrograph of basic formulation 4g with 0.75% of 'defloculating' polymer A-11. The individual character of the lamellar droplets, i.e. the 'defloculating' effect of the polymer, is beautifully demonstrated. Compare with Photograph 7.

THIS PAGE BLANK (USPTO)